Contract N6ori–107, T. O. I.
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Technical Report No. 9

Duke University
Department of Physics

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Technical Report No. 9

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CONTENTS

Der Einfluß der Schwingung auf verbotene Elektronenübergänge.

Von

H. Sponer und K. F. Herzfeld.

Bei Molekülen mit hoher Symmetrie kommt es vor, daß gewisse Elektronenübergänge an sich verboten sind, durch überlagerte Schwingungen aber schwach erlaubt gemacht werden. Hierher gehört z. B. die Benzolabsorption um 2600 Å. Der Effekt der Schwingung ist zweifach: a) Die Kerne werden verschoben; b) dadurch werden die Koeffizienten in der Elektronenwellenfunktion geändert. In dieser Arbeit wird Effekt a) allein berechnet, aber als viel zu schwach gefunden. Der Hauptteil der Intensität rührt daher von b) her.

1. Problemstellung.

Die Matrizenelemente des Übergangsmoments eines Elektronenübergangs

$$M = \int \Psi_{\mathrm{el}}'^{*} \, M \, \Psi_{\mathrm{el}}'' \, d\tau$$

hängen von der Kernkonfiguration ab, d. h. sie ändern sich mit den Kernverschiebungen. Für kleine Verschiebungen kann man M in eine Potenzreihe nach dem Normalkoordinaten ξ_s entwickeln.

$$M = M_0 + \sum M_s \, \xi_s + \sum \sum M_{s\,k} \, \xi_s \, \xi_k + \cdots .$$

Wenn M_0 von Null verschieden ist, hängt das Moment nicht wesentlich von den Kernverschiebungen ab. Dann sind Schwingungsübergänge $v \to v$ erlaubt. Dies tritt ein, wenn das direkte Produkt der Transformationseigenschaften der drei Faktoren Ψ', Ψ'' und M einen total symmetrischen Term enthält.

Ist dagegen der in ξ lineare Summand der erste Term in M, dann sind Schwingungsübergänge $v \to v$ verboten, und man erhält Dipolübergänge, die erst durch die Schwingung erlaubt gemacht werden.

Im besonderen entspricht die Absorptionsbande des Benzoldampfs um 2600 Å einem verbotenen Übergang[1,2], da die Wellenfunktion des Grundzustandes hexagonale, die des erregten Zustandes trigonale Symmetrie hat. Die Bande, der ein f-Wert von 0,0016 zukommt, wird durch die Überlagerung der Schwingung mit Wellenzahl 520 (im erregten Zustand) erlaubt gemacht[3]. Eine Schwingung kann einen Übergang

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[1] Sklar, A. L.: J. Chem. Phys. 5, 669 (1937).

[2] Goeppert-Mayer, M., u. A. L. Sklar: J. Chem. Phys. 6, 645 (1938).

[3] Sponer, H., G. Nordheim, A. L. Sklar u. E. Teller: J. Chem. Phys. 7, 207 (1939).

nur dann erlaubt machen, wenn die Wellenfunktion *nicht* als Produkt der Elektronen- und Schwingungswellenfunktion dargestellt werden kann. In dieser Arbeit soll untersucht werden, ob man diesen Effekt quantitativ berechnen kann.

2. Allgemeine Theorie.

Wir betrachten im allgemeinen ein ebenes Molekül, in welchem nur Kohlenstoffatome an der Absorption beteiligt sind. Der Elektronenübergang soll zwischen Zuständen erfolgen, die sich nur durch verschiedene lineare Kombination der atomaren Wellenfunktionen unterscheiden, und keine atomare Erregung voraussetzen.

Wir berücksichtigen ferner nur die π-Elektronen, und im besonderen nur dasjenige, welches erregt wird. Als Methode wählen wir die der Molekülwellenfunktion, in der die Molekülwellenfunktion linear aus Atomwellenfunktionen zusammengesetzt wird (in der amerikanischen Literatur als LAO-MO bezeichnet). Da als Atomfunktion $2p$ Wasserstofffunktionen benützt werden, schreiben wir für die Elektronenfunktion des Grundzustandes

$$\Psi'' = \sum a_j p_j \tag{1}$$

für den angeregten Zustand

$$\Psi' = \sum b_k p_k, \tag{2}$$

wo die a, b Koeffizienten sind und die Indizes sich auf das j-te, bzw. k-te Atom beziehen.

Es bezeichne $\vec{R_j}$ die Ruhelage des j-ten Kernes, $\vec{\Delta R_j}$ (die x-Komponente sei ΔX) seine Verschiebung durch die Schwingung; $\varphi(Q)$ sei die Schwingungswellenfunktion der betrachteten Eigenschwingung, $d\tau$ das Element der Elektronenkoordinaten. Wir nehmen nun an, daß die Schwingung die Koeffizienten a, b der Elektronenwellenfunktion *nicht* ändert, sondern nur die Lage der p-Funktionen im Raum. Dann ist die gesamte Wellenfunktion im erregten Zustand für den Schwingungsübergang $0 \to 1$,

$$\Psi' = \varphi^{(1)}(Q) \sum b_k p_k (\vec{R_k} + \vec{\Delta R_k}), \tag{3}$$

wobei die Klammer hinter den p_k die Lage des k-ten Kerns angibt. Die Kopplung kommt so zustande, daß ΔR in der Elektronenwellenfunktion auftritt.

Man hat nun als Moment in der x-Richtung[1], dividiert durch die Elektronenladung,

$$\left.\begin{aligned}\frac{1}{e} M(x, 0, 1) &= \int \Psi' \, x \, \Psi''^* \, d\tau \\ &= \sum \sum a_j^* b_k \int \varphi^{(0)}(Q) \, \varphi^{(1)}(Q) \, dQ \int p_j(\vec{R_j}) \, x \, p_k(\vec{R_k} + \vec{\Delta R_k}) \, d\tau.\end{aligned}\right\} \tag{4}$$

---

[1] Man zeigt leicht, indem man zeitabhängige Wellenfunktionen benützt, daß (4) zum richtigen Übergang gehört.

In $M(x, 0, 1)$ ist x ein Index, nicht ein Argument. Man schreibt nun

$$p_k(\vec{R} + \vec{\Delta R_k}) = p_k(\vec{R_k}) + (\vec{\Delta R_k} \cdot \operatorname{Grad} p_k),\tag{5}$$

wo Grad sich auf die Kernverschiebung bezieht.

Wir wollen nun die Integrale

$$\int p_j\, x\, p_k\, d\tau$$

berechnen und dabei den Teil, der nicht von der Verschiebung herrührt und daher nach Summation null ergibt, gleich weglassen. Man muß den Fall $k = j$ und $k \neq j$ unterscheiden. Im ersten Fall ist

$$\begin{aligned}
\int p_k\, x\, (\vec{\Delta R_k} \cdot \operatorname{Grad} p_k)\, d\tau &= \tfrac{1}{2} \int x\, (\vec{\Delta R_k} \cdot \operatorname{Grad} p_k^2)\, d\tau \\
&= -\tfrac{1}{2} \int x\, (\vec{\Delta R_k} \cdot \operatorname{grad} p_k^2)\, d\tau.
\end{aligned}\tag{6}$$

Hier bezieht sich grad auf die Elektronenkoordinaten und die Beziehung folgt, da in p die Differenz von Elektronen- und Kernkoordinaten auftritt. Durch partielle Integration sieht man dann leicht, daß (6) gleich

$$\tfrac{1}{2}\Delta X_k$$

wird.

Für $k \neq j$ bezeichne man mit x_{jk} den Mittelwert der x-Koordinate von Kern k und Kern j und schreibe

$$x = x_{jk} + \xi.$$

Dann folgt aus der Symmetrie der p-Funktionen, daß

$$\int p_j\, x\, p_k\, d\tau = x_{jk} \int p_j p_k\, d\tau = x_{jk} S_{jk},\tag{7}$$

wo S_{jk} das Überlappungsintegral ist.

Der Effekt einer Verschiebung von Kern k auf den Ausdruck (7) ist zweifach: Erstens wird x_{jk} um $\tfrac{1}{2}\Delta X_k$ verändert; zweitens wird das Überlappungsintegral um

$$\frac{dS_{jk}}{dr_{jk}} \cdot \Delta r_{jk} = S' \Delta r_{jk}$$

geändert, wobei Δr_{jk} die Änderung des Abstandes $j - k$ ist.

Daher wird schließlich:

$$\int p_j\, x\, (\Delta R_k \cdot \operatorname{Grad} p_k)\, d\tau = \tfrac{1}{2}\Delta X_k + x_{jk} S'_{jk}\Delta r_{jk}.\tag{8}$$

Man definiere nun zwei Gruppen von Konstanten, die die Verschiebungen bei der betrachteten Eigenschwingung mit der Normalkoordinate Q verbinden:

$$\begin{aligned}
\Delta X_k &= \beta_k Q \\
\Delta r_{jk} &= \gamma_{jk} Q.
\end{aligned}\tag{9}$$

Ferner ist eine Masse m_s dadurch definiert, daß die kinetische Energie der Schwingung gleich

$$\tfrac{1}{2} \sum m_k (\varDelta \dot{X}_k^2 + \varDelta \dot{Y}_k^2 + \varDelta \dot{Z}_k^2) = \tfrac{1}{2} m_s \dot{Q}^2$$

ist. v_s sei die Frequenz der Schwingung.

Dann wird

$$\left. \begin{aligned} \frac{1}{e} M(x, 0, 1) &= \Bigl[\frac{1}{2} \sum a_k^* b_k \beta_k + \sum_j \sum_{k \neq j} a_j^* b_k \times \\ &\quad \times \Bigl(\frac{1}{2} \beta_k S_{jk} + \gamma_{jk} x_{jk} S'_{jk} \Bigr) \Bigr] \int \varphi^{(0)}(Q)\, Q\, \varphi^{(1)}(Q)\, dQ \\ &= \bigl[\ \bigr] \frac{1}{2\pi} \Bigl(\frac{h}{2 m_s v_s} \Bigr)^{\frac{1}{2}}. \end{aligned} \right\} \quad (10)$$

Sei v die Frequenz, die dem Elektronenübergang entspricht, m_e die Elektronenmasse, so ist bekanntlich die gesuchte Elektronenzahl f gegeben durch

$$f = \frac{8\pi^2 m_e v}{3h} \left| \frac{1}{e} M(x, 0, 1) \right|^2,$$

also

$$f = \frac{m_e}{m_s} \frac{v}{v_s} \frac{1}{12} \left| \Bigl[\sum a_k^* b_k \beta_k + \sum_j \sum_{k \neq j} a_j^* b_k (\beta_k S_{jk} + 2\gamma_{jk} x_{jk} S'_{jk}) \Bigr] \right|^2. \quad (11)$$

3. Anwendung auf Benzol.

Wir wollen nur die Wechselwirkungen mit nächsten Nachbarn in Betracht ziehen. Alle Abstände zwischen nächsten Nachbarn sind gleich (Abstand r), die Überlappungsintegrale

$$S = 0{,}26 \qquad r S' = -0{,}587.$$

Die Klammer in (11) wird dann

$$\left. \begin{aligned} [\ ] &= \sum a_k^* b_k \beta_k + S \sum (a_{k-1}^* + a_{k+1}^*) b_k \beta_k + 2r S' \times \\ &\quad \times \sum \Bigl\{ a_{k-1}^* \frac{1}{2r} (x_{k-1} + x_k) \gamma_{k-1,k} + a_{k+1}^* \frac{1}{2r} (x_{k+1} + x_k) \gamma_{k+1,k} \Bigr\} \end{aligned} \right\} \quad (12)$$

ein, worin die x_k die ungestörten Koordinaten der Atome k sind.

Ferner führe man die radialen und tangentiellen Komponenten der Verschiebung des k-ten Atoms ein, $\varrho_k Q$ und $\sigma_k Q$, die letztere positiv für einen Rechtsumlauf.

Dann hat man als Komponenten für γ

$$\gamma_{k-1,k} = \gamma_{k+1,k} = \varrho_k \sin \frac{\pi}{3} = \frac{1}{2} \varrho_k$$

$$-\gamma_{k-1,k} = \gamma_{k+1,k} = \sigma_k \cos \frac{\pi}{3} = \frac{1}{2} \sqrt{3}\, \sigma_k.$$

Die Vorzeichen bedeuten, daß eine radiale Bewegung beide anliegenden Bindungen streckt, während tangentielle Bewegung die eine streckt, die andere zusammendrückt. Der letzte Summenausdruck in (12) wird dann

$$\frac{1}{2} r\, S' \sum \left\{ a^*_{k-1}\frac{x_{k-1}}{r} + a^*_{k+1}\frac{x_{k+1}}{r} + (a^*_{k-1}+a^*_{k+1})\frac{x_k}{r} \right\} b_k \varrho_k + \\ + \frac{1}{2} r\, S' \sum \left\{ -a^*_{k-1}\frac{x_{k-1}}{r} + a^*_{k+1}\frac{x_{k+1}}{r} + (a^*_{k-1}+a^*_{k+1})\frac{x_k}{r} \right\} b_k \sigma_k \sqrt{3}. \quad (13)$$

Dieser Ausdruck soll nun auf den Elektronenübergang bei 2600Å angewandt werden. Nach GOEPPERT-MAYER und SKLAR[1] ist das Moment die Differenz zweier Größen[2]: Die erste entspricht dem Übergang eines Elektrons von der Einelektronenfunktion Φ_{-1} zu Φ_{+2}, die zweite, dem Übergang von Φ_{+1} zu Φ_{-2}. Seien N_1, N_2 die Normierungsfaktoren, dann hat man, von einem Faktor $(2N_1 N_2)^{-\frac{1}{2}}$ für die Produkte abgesehen, die folgenden Werte für a und b

$$\Phi_{-1}\quad a^*_k = \exp\left(i\frac{\pi}{3}k\right) \qquad \Phi_{+1}\quad a^*_k = \exp\left(-i\frac{\pi}{3}k\right)$$
$$\Phi_2\quad b_k = \exp\left(i\frac{\pi}{3}2k\right) \qquad \Phi_{-2}\quad b_k = \exp\left(-i\frac{\pi}{3}2k\right).$$

Daher ist

$$a^*_k b_k = 2i\sin\pi k = 0$$
$$(a^*_{k-1}+a^*_{k+1}) b_k = 4i\sin\pi k\cos\frac{\pi}{3} = 0$$
$$(-a^*_{k-1}+a^*_{k+1}) b_k = 4i\cos\pi k\sin\frac{\pi}{3} = 2i(-1)^k.$$

Um die übrigen Terme einfach auszudrücken, ersetzen wir x_k durch $x_k \pm i y_k$. Dann ist

$$\frac{1}{r}(x\pm i y)_k = \exp \pm i\frac{\pi}{6}(5-2k),$$

und daher

$$(x\pm i y)_{k-1} = (x\pm i y)_k \exp\left(\mp i\frac{\pi}{3}\right).$$

Man erhält

$$a^*_{k-1}(x\pm i y)_{k-1}b_k + a^*_{k+1}(x\pm i y)_{k+1}b_k$$
$$= \pm(-1)^k\left(2i\sin\frac{\pi}{3}\right)^2(x\pm i y)_k = \mp 3(-1)^k(x\pm i y)_k.$$

Für $-a^*_{k-1}$ statt $+a^*_{k-1}$ wird die rechte Seite

$$(-1)^k 2i\sin\frac{2\pi}{3}(x\pm i y)_k = (-1)^k\sqrt{3}\,i(x\pm i y)_k.$$

[1] GOEPPERT-MAYER, M. u. A. L. SKLAR: J. Chem. Phys. 6, 645 (1938).
[2] Wenn man die Antisymmetrisierung vollständig durchführt, erhält man noch andere Terme, die aber höhere Potenzen der Verschiebungen enthalten.

Daher wird in (12), abgesehen von der Phase

$$[\,] = \frac{3}{2}\, r\, S' \sum (-1)^k \frac{1}{r}\, (x \pm i\, y)_k \left\{ \mp \varrho_k + \left(1 + \frac{2}{\sqrt{3}}\right) i\, \sigma_k \right\}. \quad (13')$$

Man hat ferner $2 N_1 N_2 = 96 \cdot 1{,}739$, $\nu = 38610$, $\nu_s = 520$ Wellenzahlen. Bezeichne M_s die effektive Masse der Schwingung in Molekulargewichtseinheiten; dann ist (11)

$$f = \frac{1{,}56 \cdot 10^{-5}}{M_s} \left| \sum (-1)^k \left(\exp \mp i\, \frac{\pi}{3}\, k\right) \left\{ \mp \varrho_k + \left(1 + \frac{2}{\sqrt{3}}\right) i\, \sigma_k \right\} \right|^2. \quad (14)$$

Die verschiedenen Schwingungen, die den Übergang erlaubt machen, setzen sich aus den radialen und tangentiellen Schwingungen mit verschiedenen Koeffizienten zusammen. Daher schreibt man zweckmäßig

$$\varrho_k = \frac{\varrho_k}{\varrho}\, \varrho\,, \qquad \sigma_k = \frac{\sigma_k}{\sigma}\, \sigma\,,$$

wobei ϱ_k/ϱ; σ_k/σ durch die Symmetriekoordinate bestimmt ist, während ϱ und σ die Koeffizienten sind, mit denen die Symmetriekoordinaten in der Normalkoordinate auftreten. Dann wird

$$f = \frac{1{,}56 \cdot 10^{-5}}{M_s} \left| \varrho \left\{ \sum (-1)^k \left(\pm i \exp \mp i\, \frac{\pi}{3}\, k \right) \frac{\varrho_k}{\varrho} \right\} + \left(1 + \frac{2}{\sqrt{3}}\right) \sigma \left\{ \sum (-1)^k \left(\exp \mp i\, \frac{\pi}{3}\, k\right) \frac{\sigma_k}{\sigma} \right\} \right|^2. \quad (15)$$

Bei den Schwingungen, die uns interessieren, nimmt jedes H praktisch starr an der Schwingung des betreffenden C Atoms teil, so daß man Gruppen des „Atom"-Gewichts 13 hat. Zur Bestimmung von M_s schreibt man die kinetische Energie

$$\frac{1}{2} M_s \dot{Q}^2 = \frac{1}{2}\, 13 \sum (\varrho_k^2 + \sigma_k^2)\, \dot{Q}^2$$

$$M_s = 13 \left\{ \varrho^2 \sum \left(\frac{\varrho_k}{\varrho}\right)^2 + \sigma^2 \sum \left(\frac{\sigma_k}{\sigma}\right)^2 \right\}. \quad (16)$$

Nach Craig[1] hat man für die Symmetriekoordinaten

$$\frac{\varrho_k}{\varrho} : 0,\ -1,\ +1,\ 0,\ -1,\ +1, \qquad 2\frac{\sigma_k}{\sigma} : -2,\ +1,\ +1,\ -2,\ +1,\ +1$$

d. h.

$$M_s = 52\, (\varrho^2 + \tfrac{3}{4}\, \sigma^2).$$

Die Ausrechnung ergibt

$$f = 3 \cdot 10^{-7} \frac{\left[2\sqrt{3}\, \varrho + \left(1 + \frac{2}{\sqrt{3}}\right) \sigma\right]^2}{\varrho^2 + \frac{3}{4}\, \sigma^2} = 3{,}6 \cdot 10^{-6} \frac{\left[\varrho + \left(\frac{1}{3} + \frac{1}{2\sqrt{3}}\right) \sigma\right]^2}{\varrho^2 + \frac{3}{4}\, \sigma^2}. \quad (17)$$

Nach Craig[1] ist für die 520 Schwingung $\varrho = 0{,}9$, $\sigma = -0{,}25$.

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[1] Craig, P.: J. Chem. Soc. **1950**, 59.

Eingesetzt in (17) ergibt sich

$$f = 2{,}1 \cdot 10^{-6}.$$

Nicht nur ist dieser Wert um einen Faktor 700 zu klein, sondern unsere Rechnung ergibt auch für die Einwirkung der 1572 Schwingung einen f-Wert derselben Größenordnung. Da hier die Wellenzahl ν_s dreimal so groß ist, ist der Faktor in (17) durch 3 zu dividieren. Ferner ist nach CRAIG $\varrho = 0{,}44$, $\sigma = 0{,}52$.

Man erhält

$$f = 0{,}8 \cdot 10^{-6}.$$

Experimentell ist aber für diese Schwingung der f-Wert etwa 100 mal kleiner als der für die erst behandelte.

4. Schlußfolgerungen.

Aus dem Vorangehenden muß man schließen, daß der hier behandelte Effekt nur einen kleinen Beitrag zum Übergangsmoment liefert, und daß der Hauptanteil von der Änderung[1] der Koeffizienten (b_k) in der Wellenfunktion herrührt, eine Änderung, die durch die von der Schwingung verursachten Abstandsänderungen bedingt wird. Tatsächlich hat CRAIG[2] eine befriedigende Abschätzung von f dadurch erreicht, daß er eine Beimischung des erregten Zustandes E_u^- (erlaubter Übergang 1800 Å) in den Zustand B_{2u} durch die Schwingung berechnet. Eine solche Beimischung bedeutet aber eine Änderung der Koeffizienten b.

Der f-Wert der Dipolstrahlung, die von der $0 \rightarrow 1$ Schwingung herrührt, ist dann

$$f = \frac{m_e}{3 m_s} \frac{\nu}{\nu_s} \left| \sum_k \{a_k^* (x \pm i\,y)_k + S\,[a_{k-1}^* (x \pm i\,y)_{k-1} + \\ + a_{k+1}^* (x \pm i\,y)_{k+1}]\} \frac{d b_k}{dQ} \right|^2. \tag{18}$$

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[1] HERZBERG, G., u. E. TELLER: Z. phys. Chem. Abt. B **21**, 410 (1933).

[2] CRAIG, P.: J. Chem. Soc. **1950**, 59.

On the Molecular-Orbital Theory of Conjugated Organic Compounds with Application to the Perturbed Benzene Ring

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On the Molecular-Orbital Theory of Conjugated Organic Compounds with Application to the Perturbed Benzene Ring*

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The electronic structure of a molecular system is investigated by using the idea of molecular orbitals. The behavior of the separate molecular orbitals and the orbital energies under the influence of the substitution of one or more heteroatoms, considered as perturbations, is examined. A series of quantities, separate charge orders, bond orders, and mutabilities are introduced, giving information about some characteristic physical and chemical properties of the compound. The perturbation scheme is carried out explicitly to the second order in the energies and to the first order in the orbitals, and special attention is paid to the treatment of degenerate levels. The overlapping problem is fully discussed. The basic results are independent of any empirical parameters, and they may be used either in the naïve semi-empirical theory or in a more elaborate theoretical approach based on an antisymmetrized molecular wave function.

As an example, numerical applications are carried out in detail on benzene. Separate charge orders, bond orders, and mutabilities are tabulated, and orbital energies for a perturbed benzene ring with one or two heteroatoms are explicitly given.

INTRODUCTION

THE molecular orbital theory for treating properties of molecules, developed by Lennard-Jones, Hund, and Mulliken, was first applied to the aromatic organic compounds by Hückel[1] in his investigation of the mobile electrons of the benzene ring. Hückel[2] was also interested in the problem of the change of the electronic structure caused by the introduction in the ring of a heteroatom or a substituent, which he considered as perturbations. However, Hückel's mathematical results concerning the directing power of such a perturbation were given their correct chemical interpretation first by Wheland and Pauling,[3] who further developed the theory.

The whole approach had a *semi-empirical* character, since the fundamental integrals were considered as adjustable parameters which had to be found from observed data, and the whole theory was, therefore, essentially a device for correlating one set of experimental data with another. This naïve molecular theory has been successful in treating the ground state of the aromatic molecules and conjugated systems in general, describing the connection between such quantities as electron affinities, resonance energies, ionization energies, dipole moments, bond lengths, etc., and explaining the fundamental chemical law of alternating polarity.[4]

A general theory of the electronic structure of conjugated systems based on these ideas has later been developed by Coulson and Longuet-Higgins.[5] By introducing the new and useful concepts of total charge orders, bond orders, and mutual polarizabilities of all the mobile electrons, they could obtain valuable information particularly about such properties of the molecule as are independent of the adjustable parameters. Their theory was still based on the "naïve" assumption that the total energy of the mobile electrons could be derived simply by summing the orbital energies of all occupied orbitals,[6] and the basic quantities mentioned above could then be obtained as the first and second derivatives of this energy with respect to the perturbation integrals.

Although the naïve theory has been remarkably successful in treating the ground state of the conjugated compounds, it has usually failed when one has tried to extend it to the excited states. There are also other strong indications that a more exact theory would be desirable. It is well known that a better theoretical approach can be based on an antisymmetrized molecular wave function, which is approximated by a determinant or a sum of determinants constructed from molecular spin orbitals. We note that, in this case, the molecular orbitals and the orbital energies play still a fundamental role,[7] but that the sum of the orbital energies involved has lost its simple physical meaning. This implies that it is probably just as important to investigate the separate orbital energies and their derivatives with respect to the perturbation integrals as it was to consider the "total" quantities, obtained by simply summing the contributions from all the mobile electrons.

The purpose of this paper is therefore to give a theory

[1] E. Hückel, Z. Physik **70**, 204 (1931).
[2] E. Hückel, Z. Physik **72**, 310 (1931); **76**, 628 (1932).
[3] G. W. Wheland and L. Pauling, J. Am. Chem. Soc. **57**, 2091 (1939). See also G. W. Wheland, J. Am. Chem. Soc. **64**, 902 (1942), and H. C. Longuet-Higgins and C. A. Coulson, Trans. Faraday Soc. **43**, 87 (1947).
[4] A survey of the development of the theory, treating mostly bond lengths but also other properties, has recently been given by J. Lennard-Jones, Proc. Roy. Soc. (London) **A207**, 75 (1951), where also a list of references may be found.

[5] C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) **A191**, 39; **192**, 16 (1947); **193**, 447, 456; **195**, 188 (1948).
[6] Compare V. Fock, Z. Physik **61**, 126 (1930); see also R. G. Parr, J. Chem. Phys. **19**, 799 (1951).
[7] Compare also the band theory of crystals.

of the mobile electrons of a conjugated system, which is a generalization of the ideas introduced by Coulson and Longuet-Higgins, but where, instead of the naïve total energy and its derivatives, we will investigate the behavior of the separate molecular orbitals and orbital energies under the influence of a perturbation caused by the substitution in the system of one or more hetero-atoms. We will define a series of quantities, separate charge orders, bond orders, and mutabilities, which can be derived from the orbital energies in the same way as the total quantities could be derived from the previous "total energy." In this case, particular attention has to be paid to the treatment of the *degenerate* levels, i.e., the molecular orbitals having the same orbital energy, and, for this purpose, we will use a special perturbation scheme which was recently described by the author. The perturbation treatment will be carried out explicitly to the second order in the energies and to the first order in the orbitals.

The results obtained are independent of all adjustable parameters, and we note that they can be used in the naïve semi-empirical theory as well as in a more elaborate theory based on an antisymmetrized molecular wave function. In this paper, we will consider only the problem of calculating the separate molecular orbitals and orbital energies by using perturbation theory, and the question, how these orbitals should be properly combined in order to correspond to the various molecular states, will be treated in a later publication.[8]

As an example of the theory, numerical applications will be carried out in detail on the perturbed benzene ring. Separate charge orders, bond orders, and mutabilities will be tabulated, and the orbital energies for a ring perturbed by one or two heteroatoms will be explicitly given.

PART I. ON THE GENERAL MOLECULAR-ORBITAL THEORY OF CONJUGATED SYSTEMS

1. The Effective Hamiltonian and the Secular Equation; The Overlapping Problem

The molecular orbital method for treating properties of molecules is essentially based on the idea of the existence of an *effective Hamiltonian* H_{eff}, which is a one-electron operator working on the space-coordinates, $\mathbf{x} = (x_1, x_2, x_3)$, of a single electron. The physical meaning of H_{eff} is simple: it is the quantum-mechanical equivalent to the energy of a single electron moving in the potential field of the nuclear framework and of all the other electrons. The molecular orbitals $\psi(\mathbf{x})$ and the orbital energies ϵ are then given as the eigenfunctions and the eigenvalues of the Schrödinger equation

$$H_{eff}\psi = \epsilon\psi. \tag{1}$$

The idea that the behavior of each electron in a many-electron system is approximately regulated by an

effective Hamiltonian goes back to Hartree, who developed it for the atomic case. Later this idea was refined by Slater, Fock, and Dirac, showing that the effective Hamiltonian could be derived from the ordinary Hamiltonian for the total many-electron system by using the variational principle and forms of the total wave function approximated by simple products or antisymmetrized products of one-electron wave functions. In this paper we will confine ourselves to considering only closed-shell ground states, but, even in this simple case, the mathematical expression for H_{eff} is rather complicated: H_{eff} is the sum of the operator for the kinetic energy of the electron and the operator for the potential energy of the electron in the Coulomb field of the nuclei and of all electrons belonging to the system, minus the exchange operator for the electron in the field of all electrons. The effect of the exchange operator is essentially that it subtracts the interaction between the electron in a particular orbital and itself from the Coulomb potential.[9] A more detailed discussion of this subject for the molecular case will be given in another paper. Here it is sufficient that the operator H_{eff} exists and that it is the *same* for all orbitals. The last fact means also that, in the theoretical part, it is not necessary to distinguish between the different types of the orbitals.[10]

Because of the difficulty of treating the eigenvalue problem (1) exactly, we will here use the approximate MO-LCAO approach,[11] where the molecular orbitals (MO) are formed by linear combinations of the atomic orbitals (AO) associated with the molecule under consideration. These atomic orbitals ϕ_μ ($\mu = 1, 2, \cdots, n$) are here assumed to be real and normalized. Atomic orbitals belonging to the same atom are further orthogonal, and for different atoms they are overlapping with *overlap integrals* $S_{\mu\nu}$ defined by

$$S_{\mu\nu} = \int \phi_\mu \phi_\nu d\tau - \delta_{\mu\nu}. \tag{2}$$

The overlap integrals form together a matrix $\mathbf{S}$, which is real and symmetric, $S_{\mu\nu} = S_{\nu\mu}$. The fundamental quantities in the theory are the matrix elements of H_{eff} with respect to these AO:

$$H_{\mu\nu} = \int \phi_\mu H_{eff} \phi_\nu d\tau. \tag{3}$$

The quantities $H_{\mu\mu} = \alpha_\mu$ and $H_{\mu\nu} = \beta_{\mu\nu} (\mu \neq \nu)$ are in the literature usually called the Coulomb and exchange integrals, respectively, but this description is not a particularly happy one, since, among other things, H_{eff}

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[8] P. O. Löwdin, "On the basis of the molecular orbital theory of molecules" (to be published).

[9] See, for instance, J. C. Slater, Phys. Rev. **81**, 385 (1951).

[10] Compare P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930). See also F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 245.

[11] The names and abbreviations used here are mainly those introduced by Mulliken.

contains also the kinetic energy operator in addition to the electrostatic parts.

In a large part of the literature, the overlap integrals (2) have simply been neglected, but a number of authors has shown that they are in reality of fundamental importance. Here we will treat the non-orthogonality problem by using the simple scheme previously developed by the author.[12] In addition to the ordinary AO ϕ_μ, we will introduce a set of orthonormalized atomic orbitals (ON-AO) φ_μ ($\mu = 1, 2, \cdots, n$), given by the matrix formula

$$\varphi = \phi(1+S)^{-\frac{1}{2}} \qquad (4)$$

or

$$\varphi_\mu = \phi_\mu - \tfrac{1}{2}\sum_\alpha \phi_\alpha S_{\alpha\mu} + \tfrac{3}{8}\sum_{\alpha\beta} \phi_\alpha S_{\alpha\beta} S_{\beta\mu} - \cdots. \qquad (5)$$

It is easily shown that $\int \varphi_\mu \varphi_\nu d\tau = \delta_{\mu\nu}$. The ordinary AO ϕ_μ are *localized*, whereas the ON-AO φ_μ are only semi-localized; the latter orbitals have further a many-orbital character, which sometimes will lead to important physical consequences.[13] In addition to (3), we will also introduce the matrix elements

$$H_{\mu\nu}' = \int \varphi_\mu H_{\text{eff}} \varphi_\nu d\tau, \qquad (6)$$

and between $\mathbf{H}'$ and $\mathbf{H}$ there is then the matrix relation

$$\mathbf{H}' = (1+S)^{-\frac{1}{2}} \mathbf{H} (1+S)^{-\frac{1}{2}}. \qquad (7)$$

We have previously pointed out an interesting difference between $\mathbf{H}'$ and $\mathbf{H}$. The matrix $\mathbf{H}'$ has the fundamental property that its nondiagonal elements are invariant against an arbitrary change k of the zero-point of H_{eff}, whereas the diagonal elements all undergo the same change k. This does not apply to $\mathbf{H}$, which means that $\mathbf{H}'$ (but not $\mathbf{H}$) may have a simple physical interpretation. Following a suggestion of Chirgwin and Coulson, we will call the elements $H_{\mu\mu}' = \alpha_\mu'$ and $H_{\mu\nu}' = \beta_{\mu\nu}'(\mu \neq \nu)$ the *charge affinity* of the ON-AO μ and the *bond affinity* of the bond $\mu - \nu$, respectively. A purely theoretical evaluation of the elements of $\mathbf{H}'$ and $\mathbf{H}$ is a rather complicated mathematical problem,[14] and in the naïve theory they have, therefore, usually been determined by fitting some derived quantities to observed data. However, it may be emphasized that, due to the invariance condition pointed out above and the necessity of taking the overlap into consideration in almost all cases, it is in reality only the matrix $\mathbf{H}'$ which should be used for this fitting process.

In the following treatment, we will characterize a molecular orbital by an *upper* index j, k, $\cdots$, and an atomic orbital by a *lower* index μ, ν, $\cdots$. In the MO-

LCAO approach, the molecular orbitals ψ^j are formed by linear combination of the given AO or of the ON-AO:

$$\psi^j = \sum_\mu \varphi_\mu C_\mu{}^j. \qquad (8)$$

In order to determine the values of the complex or real coefficients $C_\mu{}^j$, which correspond to the best approximation of the eigenfunctions of H_{eff}, we will use the variation principle:

$$\epsilon^j = \int \psi^{j*} H_{\text{eff}} \psi^j d\tau = \text{extreme value}, \qquad (9)$$

$$\int \psi^{j*} \psi^j d\tau = 1, \qquad (10)$$

which leads to the linear equation system

$$\sum_{\nu=1}^{n} (H_{\mu\nu}' - \epsilon^j \delta_{\mu\nu}) C_\nu{}^j = 0, \quad \mu = 1, 2 \cdots n \qquad (11)$$

where the quantities ϵ^j are the best approximations for the orbital energies, which can be obtained by this approach. The energies are determined by the condition

$$\det\{H_{\mu\nu}' - \epsilon\delta_{\mu\nu}\} = 0, \qquad (12)$$

and when this secular equation is solved, the coefficients can be found from (11). Due to the Hermitean property of H_{eff}, two MO belonging to two different values of ϵ are always orthogonal to each other. If m solutions of (12) appear to be equal, the corresponding level is degenerate, and, in this case, there exist m linearly independent solutions of (11), which may be chosen orthogonal to each other. In this way, the set of MO forms an orthonormalized system, and, since the relation (8)

$$\psi = \varphi \mathbf{C} \qquad (13)$$

represents a transformation between two orthonormalized systems, the matrix $\mathbf{C}$ of the coefficients must be a *unitary* matrix:

$$\mathbf{C}^\dagger \mathbf{C} = \mathbf{C} \mathbf{C}^\dagger = 1. \qquad (14)$$

Here we have used the notation that, if $\mathbf{A}$ is an arbitrary matrix, $\mathbf{A}^\dagger$ denotes its Hermitean adjoint matrix defined by $A_{\mu\nu}{}^\dagger = A_{\nu\mu}{}^*$.

2. Charge and Bond Orders for Individual Orbitals

In their general theory of conjugated systems, Coulson and Longuet-Higgins introduced the useful concepts of charge and bond orders of the *total* system of mobile electrons. Here we will further develop this idea by investigating the contribution to these quantities from the separate orbitals involved. In fact, separate bond orders have been treated previously by Coulson,[15] and the importance of separate charge orders has been stressed recently by Lennard-Jones[16] and by Fukui,

[12] P. O. Löwdin, Arkiv Mat. Astron. Fysik 35A, 9 (1947); *A Theoretical Investigation into Some Properties of Ionic Crystals* (thesis) (Almqvist & Wiksell, Uppsala, Sweden, 1948); J. Chem. Phys. 18, 365 (1950). Compare also B. H. Chirgwin and C. A. Coulson, Proc. Roy. Soc. (London) A201, 196 (1950).

[13] For instance, the *many-body forces* in ionic crystals; see reference 12.

[14] For a more detailed study, see reference 8.

[15] C. A. Coulson, Proc. Roy. Soc. (London) A169, 413 (1939).

[16] J. Lennard-Jones, see reference 4.

Yonezawa, and Shingu.[17] Let us therefore in greater detail consider the quantities

$$q_\mu{}^j = C_\mu{}^{j*} C_\mu{}^j, \quad p_{\mu\nu}{}^j = \tfrac{1}{2}(C_\mu{}^{j*} C_\nu{}^j + C_\nu{}^{j*} C_\mu{}^j). \quad (15)$$

According to (8), the quantity $|C_\mu{}^j|^2$ measures the fraction of the time the electron in the MO ψ^j spends in the ON–AO φ_μ, or more approximately "at the atom μ," and $q_\mu{}^j$ will therefore be called the *charge order at atom μ of the orbital j*. Following Coulson,[15] the quantity $p_{\mu\nu}{}^j$ $(\mu \neq \nu)$ will be interpreted as the *bond order of the bond $\mu - \nu$ of the orbital j*. The total charge order q_μ and the total bond order $p_{\mu\nu}$ of a complex of electrons are then found by summing over the orbitals involved:

$$q_\mu = \sum_j q_\mu{}^j, \quad p_{\mu\nu} = \sum_j p_{\mu\nu}{}^j, \quad (16)$$

giving the quantities investigated by Coulson and Longuet-Higgins.

By using (11) and its conjugate complex relation,

$$\sum_\nu H_{\mu\nu}' C_\nu{}^j = \epsilon^j C_\mu{}^j, \quad \sum_\nu H_{\mu\nu}' C_\nu{}^{j*} = \epsilon^j C_\mu{}^{j*},$$

and multiplying the first with $C_\mu{}^{j*}$ and the second with $C_\nu{}^j$. we obtain a formula for the connection between the separate charge and bond orders:

$$\sum_{\nu \neq \mu} H_{\mu\nu}' p_{\mu\nu}{}^j = (\epsilon^j - H_{\mu\mu}') q_\mu{}^j. \quad (17)$$

A similar simple relation for the total quantities does not exist.

We note that there is also a close connection between the quantities (15) and the orbital energies. From (9), (8), and (6), it follows

$$\epsilon^j = \sum_{\mu\nu} C_\mu{}^{j*} H_{\mu\nu}' C_\nu{}^j. \quad (18)$$

Let us first consider a *nondegenerate* level, and let us assume that each element $H_{\mu\nu}'$ obtains an independent symmetric variation $dH_{\mu\nu}' = dH_{\nu\mu}'$. According to (11) and (12), both the orbital energy ϵ^j and the coefficients $C_\mu{}^j$ are then changed by infinitesimal quantities, and, by taking the derivative of (18) with respect to $H_{\mu\nu}'$ and by using (11) and the normalization condition, we obtain for every nondegenerate level j:

$$q_\mu{}^j = \frac{\partial \epsilon^j}{\partial H_{\mu\mu}'}, \quad p_{\mu\nu}{}^j = \frac{1}{2} \frac{\partial \epsilon^j}{\partial H_{\mu\nu}'}, \quad (\mu \neq \nu). \quad (19)$$

From (18) we get by a second derivation

$$\frac{\partial q_\mu{}^j}{\partial H_{\kappa\kappa}'} = \frac{\partial^2 \epsilon^j}{\partial H_{\kappa\kappa}' \partial H_{\mu\mu}'} = \frac{\partial q_\kappa{}^j}{\partial H_{\mu\mu}'};$$

$$\frac{\partial q_\mu{}^j}{\partial H_{\kappa\lambda}'} = \frac{\partial^2 \epsilon^j}{\partial H_{\kappa\lambda}' \partial H_{\mu\mu}'} = 2 \frac{\partial p_{\kappa\lambda}{}^j}{\partial H_{\mu\mu}'};$$

$$\frac{\partial p_{\mu\nu}{}^j}{\partial H_{\kappa\lambda}'} = \frac{1}{2} \frac{\partial^2 \epsilon^j}{\partial H_{\kappa\lambda}' \partial H_{\mu\nu}'} = \frac{\partial p_{\kappa\lambda}{}^j}{\partial H_{\mu\nu}'}. \quad (20)$$

[17] Fukui, Yonezawa, and Shingu, J. Chem. Phys. **20**, 722 (1952).

This gives the following three reciprocity theorems: For a given nondegenerate level j, the change of the charge order of an atom μ with respect to the change of the charge affinity of the atom κ equals the change of the charge order of the atom κ with respect to a change of the charge affinity of the atom μ; the change of the charge order of an atom μ with respect to a change of the bond affinity of the bond $\kappa - \lambda$ is twice the change of the bond order of the bond $\kappa - \lambda$ with respect to the change of the charge affinity of the atom μ; and, finally, the change of the bond order of the bond $\mu - \nu$ with respect to a change of the bond affinity of the bond $\kappa - \lambda$ equals the change of the bond order of the bond $\kappa - \lambda$ with respect to a change of the bond affinity of the bond $\mu - \nu$.

The corresponding theorems for the total quantities were first stated by Coulson and Longuet-Higgins.[5]

The treatment of a *degenerate* energy level ϵ^j is somewhat more complicated due to the ambiguity in the choice of the eigenfunctions. Let m^J be the order of the degeneracy, and let further (J) denote the class of all molecular orbitals associated with the eigenvalue ϵ^j. In order to describe this class, we will use an orthonormalized set of m^J orbitals $j', j'', j''', \cdots$ etc., which is determined except for a unitary transformation. We note that, for each orbital of this set, the quantities $q_\mu{}^j$ and $p_{\mu\nu}{}^j$ formally exist according to (15), but that they cannot have any direct physical interpretation, since they are not invariant against unitary transformations within the class (J). However, by summing once over the contributions from all indices $j', j'', j''', \cdots$, we get quantities

$$q_\mu{}^J = \sum_j^{(J)} q_\mu{}^j = \sum_j^{(J)} C_\mu{}^j C^{\dagger j}{}_\mu,$$

$$p_{\mu\nu}{}^J = \sum_j^{(J)} p_{\mu\nu}{}^j = \frac{1}{2} \sum_j^{(J)} (C_\mu{}^j C^{\dagger j}{}_\nu + C_\nu{}^j C^{\dagger j}{}_\mu), \quad (21)$$

which have the desired invariance property and consequently are independent of the particular reference set. These quantities $q_\mu{}^J$ and $p_{\mu\nu}{}^J$ will be called the *total charge orders* and the *total bond orders* of the degenerate level J, respectively. By treating the energy sum

$$\epsilon^J = \sum_j^{(J)} \epsilon^j = m^J \epsilon^j \quad (22)$$

in the same way as (18), we then easily obtain

$$q_\mu{}^J = \frac{\partial \epsilon^J}{\partial H_{\mu\mu}'}, \quad p_{\mu\nu}{}^J = \frac{1}{2} \frac{\partial \epsilon^J}{\partial H_{\mu\nu}'}, \quad (\mu \neq \nu). \quad (23)$$

The treatment of a real degeneracy usually does not render any serious difficulty. The problem is instead to find the eventual splitting of a degenerate level under the influence of a perturbation.

In this connection, a few words may be said about the use of *complex* coefficients $C_\mu{}^j$ in forming the molecular orbitals. The effective Hamiltonian H_{eff} is always Hermitean, but, in most molecular application it is also *real*. The absence of the imaginary unit i in H_{eff} means that all its eigenfunctions can be represented in a real form. For a nondegenerate level, it is usually simplest to use the real description, since a complex factor is entirely without importance and vanishes automatically in forming, e.g., the quantities (15). For a degenerate level, it may sometimes be feasible to consider a complex description[18] of the class (J), but even in such a case the complex reference set can be derived from a real reference set by a unitary transformation. This implies that the sum,

$$\sum_j^{(J)} C_\mu{}^j C_\nu{}^{j*} = \sum_j^{(J)} C_\mu{}^j C^{\dagger j}{}_\nu, \tag{24}$$

is always *real*, since it is real for a real reference set and it is further invariant against unitary transformations within the class (J); see Eq. (60). We have, therefore,

$$\sum_j^{(J)} C_\nu{}^j C_\mu{}^{j*} = (\sum_j^{(J)} C_\mu{}^j C_\nu{}^{j*})^* = \sum_j^{(J)} C_\mu{}^j C_\nu{}^{j*}, \tag{25}$$

and the symmetrization in the second of the relations (21) is therefore in reality unnecessary.

Finally, we observe that the quantities (15) are only special elements of a more general matrix

$$d_{\mu\nu}{}^{jk} = \tfrac{1}{2}(C_\mu{}^{j*}C_\nu{}^k + C_\nu{}^{j*}C_\mu{}^k), \tag{26}$$

which will be called the *complete charge and bond order matrix* with respect to pairs of individual orbitals. This matrix fulfills the symmetry relations

$$d_{\mu\nu}{}^{jk} = d_{\nu\mu}{}^{jk}, \quad d_{\mu\nu}{}^{kj} = (d_{\mu\nu}{}^{jk})^*. \tag{27}$$

According to (15) and (26), we have further

$$q_\mu{}^j = d_{\mu\mu}{}^{jj}, \quad p_{\mu\nu}{}^j = d_{\mu\nu}{}^{jj}, \quad (\mu \neq \nu), \tag{28}$$

which means that the separate charge and bond orders are particular elements of the matrix $\mathbf{d}^{jk}$ for $j=k$.

The quantities (15) and (26) are useful both in the "naïve" MO-theory and in a more elaborate theoretical treatment of a molecular system. In the semi-empirical theory, the *total charge orders* were used already by Wheland and Pauling[3] for investigating the chemical reactivities of the various atoms of a conjugated system, and recently some authors[4,17] have stressed the special importance for this problem of the charge orders of the *frontier* electrons, i.e., the electrons occupying the orbital with the highest energy. All these treatments have been based on a semi-empirical assumption concerning the connection between the charge orders and the reactivities. For this connection the relations (19)

may be of fundamental importance. Following Coulson and Longuet-Higgins,[5] we wish to emphasize that it is probable that a closer examination of the connection between the (total and frontier) orbital energies and the reaction energies would give a deeper theoretical understanding of the substitution process, since the charge order for an atom in a specific position gives just the rate of the change of the orbital energy which depends on the change of the charge affinity due to the approach of a substituent.

Sometimes the separate charge and bond orders or the total quantities may be evaluated by special simple rules,[19] and in such cases the corresponding orbital energies may be found by using the relations (19) in a reverse way. Longuet-Higgins[19] has used this reverse process for treating some energy problems in heteroaromatic compounds.

In the semi-empirical theory, the *total bond orders* have been used by Coulson and Longuet-Higgins[5] for determining the bond lengths and the force constants in conjugated systems.

We note that, independent of the interpretation of the separate or total charge and bond orders in the semi-empirical theory, the quantities $d_{\mu\nu}{}^{jk}$ given by (26) are of essential importance also in a more elaborate theoretical approach, since they are very useful for the simplification and systematization of the mathematical expressions involved.[20]

3. Perturbation Theory

Here we will investigate how the separate orbitals, orbital energies, charge orders, and bond orders are affected by the substitution in a given molecule of one or more atoms or groups, which may be considered as perturbations. Let us characterize quantities belonging to the original system by the index zero:

$$\psi^{j(0)} = \sum_\mu \varphi_\mu{}^{(0)} C_\mu{}^{j(0)}, \quad H_{\mu\nu}{}'^{(0)} = \int \varphi_\mu{}^{(0)} H_{eff}{}^{(0)} \varphi_\nu{}^{(0)} d\tau, \tag{29}$$

whereas for quantities associated with the new molecule we will use the ordinary notations:

$$\psi^j = \sum_\mu \varphi_\mu C_\mu{}^j, \quad H_{\mu\nu}{}' = \int \varphi_\mu H_{eff} \varphi_\nu d\tau. \tag{30}$$

Both the effective Hamiltonian, the atomic orbitals, the overlapping conditions, and the molecular orbitals may be changed by the substitution, but, if the two molecules under consideration are related closely enough, it is possible to treat these changes by means of perturbation theory. For this purpose we will introduce

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[15] See, for instance, the treatment of benzene in Part II.

[19] H. C. Longuet-Higgins, J. Chem. Phys. **18**, 265, 275, 283 (1950).

[20] See P. O. Löwdin, J. Chem. Phys. **19**, 1570, 1579 (1951), and reference 8.

the *perturbation integrals*

$$V_{\mu\nu} = H_{\mu\nu}' - H_{\mu\nu}'^{(0)}, \tag{31}$$

i.e., the changes in charge and bond affinities, which may be expressed as fractions of the integrals $H_{\mu\nu}'^{(0)}$. We observe that a perturbation treatment based on (31) goes beyond the conventional perturbation theory, which would consider only the operator $H_{eff} - H_{eff}^{(0)}$ as a perturbation.

According to (11) and (14), our fundamental problem is to solve the matrix equations

$$\mathbf{H'C} = \mathbf{C\varepsilon}, \quad \mathbf{C^\dagger C} = \mathbf{CC^\dagger} = 1, \tag{32}$$

where ε is the diagonal matrix formed from the unknown eigenvalues ε^i. This means that we have to find a unitary matrix $\mathbf{C}$ which transforms $\mathbf{H'}$ into diagonal form:

$$\mathbf{C^\dagger H' C} = \text{diagonal matrix}, \tag{33}$$

and the orbital energies are then determined by the diagonal row of the right-hand side matrix. For the original "unperturbed" molecule, we obtain in the same way

$$\mathbf{H'^{(0)}C^{(0)}} = \mathbf{C^{(0)}\varepsilon^{(0)}}, \quad \mathbf{C^{(0)\dagger}C^{(0)}} = \mathbf{C^{(0)}C^{(0)\dagger}} = 1. \tag{34}$$

The definition (31) gives the matrix relation

$$\mathbf{H'} = \mathbf{H'^{(0)}} + \mathbf{V}, \tag{35}$$

where $\mathbf{V}$ is the matrix of the elements $V_{\mu\nu}$. By introducing the notations

$$\mathbf{C} = \mathbf{C^{(0)}X}, \quad \mathbf{v} = \mathbf{C^{(0)\dagger}VC^{(0)}}, \tag{36}$$

and by multiplying (32) to the left by $\mathbf{C^{(0)\dagger}}$, we obtain the following perturbation equation in the MO-space:

$$(\mathbf{\varepsilon^{(0)}} + \mathbf{v})\mathbf{X} = \mathbf{X\varepsilon}, \quad \mathbf{X^\dagger X} = \mathbf{XX^\dagger} = 1. \tag{37}$$

This equation can now be solved by ordinary perturbation theory. For the treatment of a degenerate level we will use the simple scheme the author[21] recently developed by generalizing an idea given by Gora.[22] This scheme was particularly meant for applications to quantum chemistry.

Simplification of the Matrix Elements used in the Perturbation Scheme

For the sake of simplicity, let us treat here also a non-degenerate level as the simplest case of a degeneracy

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[21] P. O. Löwdin, J. Chem. Phys. **19**, 1396 (1951). The author's attention has been drawn to the existence of three recently published papers which were not available to us during the preparation of our manuscript and which we therefore would like to refer to here, namely: S. Sueoka, J. Phys. Soc. (Japan) **4**, 361 (1949); M. H. L. Pryce, Proc. Phys. Soc. (London) A**63**, 25 (1950); M. Lax, Phys. Rev. **79**, 200 A (1950). Sueoka treating the interaction between two diagonal subsystems, and Pryce and Lax investigating the degeneracy problem have obtained results similar to those given in our paper. In all these independent works, the methods of derivation are closely related to the simple idea introduced by Gora, reference 22.

[22] E. Gora, Z. Physik **120**, 121 (1942-43).

with $m^J = 1$. Let us then consider an arbitrary index j, which belongs to a degenerate class (J) of the unperturbed molecule. In order to solve the eigenvalue problem (37) by perturbation theory explicitly to the first and second orders in the eigenfunctions and eigenvalues, respectively, we will introduce the quantities

$$(j\alpha) = \varepsilon^{j(0)} - \varepsilon^{\alpha(0)}, \tag{38}$$

$$U^{jk} = \varepsilon^{j(0)}\delta^{jk} + v^{jk} + \sum_{\alpha \neq (J)} \frac{v^{j\alpha}v^{\alpha k}}{(j\alpha)}, \tag{39}$$

where, in the last term, we sum only over $\alpha \neq (J)$, i.e., we omit all terms for which $(j\alpha) = 0$. According to reference 21, the eigenvalues of the class (J) of the perturbed molecule are then given by the m^J roots of the algebraic equation:

$$\begin{vmatrix} U^{i'i'} - \varepsilon; & U^{i'i''}; & U^{i'i'''}; & \cdots \\ U^{i''i'}; & U^{i''i''} - \varepsilon; & U^{i''i'''}; & \cdots \\ U^{i'''i'}; & U^{i'''i''}; & U^{i'''i'''} - \varepsilon; & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{vmatrix} = 0. \tag{40}$$

The problem of the splitting of the levels in the class (J) is therefore solved by finding the eigenvalues of a sub-matrix $\mathbf{U}_{sub}$ of order m^J. Let further $\mathbf{X}_{sub}$ be the unitary matrix of order m^J, which transforms $\mathbf{U}_{sub}$ into diagonal form. According to reference 21, the coefficients X^{ki} in general are then given by

$$X^{ki} = \begin{cases} X_{sub}^{ki}, & k \text{ in } (J) \\ \dfrac{1}{(jk)} \sum_{\alpha = (J)} v^{ka}X_{sub}^{ai}, & k \neq (J) \end{cases} \tag{41}$$

and the perturbation problem is solved.

We are here particularly interested in the simplification of the explicit forms of the matrix elements in the relations (39)–(41). The perturbation matrix $\mathbf{V}$ in (31) is symmetric, $V_{\mu\nu} = V_{\nu\mu}$, and by using this property and (26), the perturbation matrix $\mathbf{v}$ in (36) takes the form

$$v^{jk} = \sum_{\mu\nu} C^{\dagger j}{}_\mu{}^{(0)} V_{\mu\nu} C_\nu{}^{k(0)} = \sum_{\mu\nu} V_{\mu\nu}d_{\mu\nu}{}^{jk(0)}, \tag{42}$$

which implies that the complete charge and bond order matrix $\mathbf{d}^{(0)}$ is of essential importance in the perturbation scheme. In the following we will omit the index zero on the matrix $\mathbf{d}$, if there is no possibility of misunderstanding.

For the second-order term in U^{jk} in (39), we obtain in the same way by a symmetrization

$$\sum_{\alpha \neq (J)} \frac{v^{j\alpha}v^{\alpha k}}{(j\alpha)} = \sum_{\alpha \neq (J)} \sum_{\mu\nu\kappa\lambda} V_{\mu\nu}V_{\kappa\lambda} \frac{d_{\mu\nu}{}^{j\alpha}d_{\kappa\lambda}{}^{\alpha k}}{(j\alpha)}$$

$$= \frac{1}{2} \sum_{\mu\nu\kappa\lambda} \sum_{\alpha \neq (J)} V_{\mu\nu}V_{\kappa\lambda} \frac{d_{\mu\nu}{}^{j\alpha}d_{\kappa\lambda}{}^{\alpha k} + d_{\kappa\lambda}{}^{j\alpha}d_{\mu\nu}{}^{\alpha k}}{(j\alpha)}$$

$$= \frac{1}{2} \sum_{\mu\nu\kappa\lambda} V_{\mu\nu}V_{\kappa\lambda}\pi_{\mu\nu,\kappa\lambda}{}^{jk}, \tag{43}$$

where we have introduced the notation

$$\pi_{\mu\nu,\kappa\lambda}{}^{jk} = \sum_{\alpha \neq (J)} \frac{d_{\mu\nu}{}^{j\alpha}d_{\kappa\lambda}{}^{\alpha k}+d_{\kappa\lambda}{}^{j\alpha}d_{\mu\nu}{}^{\alpha k}}{(j\alpha)}. \quad (44)$$

The quantities π fulfill the following symmetry relations:

$$\pi_{\mu\nu,\kappa\lambda}{}^{jk} = \pi_{\nu\mu,\kappa\lambda}{}^{jk}, \quad \pi_{\mu\nu,\kappa\lambda}{}^{jk} = \pi_{\kappa\lambda,\mu\nu}{}^{jk},$$
$$\pi_{\mu\nu,\kappa\lambda}{}^{kj} = (\pi_{\mu\nu,\kappa\lambda}{}^{jk})^*, \quad (45)$$

and, as we shall see later, they are closely related to the mutual polarizabilities introduced by Coulson and Longuet-Higgins.[5] Using a name proposed by Lennard-Jones[4] for quantities of this type, we will call the matrix π the *complete mutability matrix*.

By using (42) and (43), the fundamental matrix element U^{jk} given by (39) can now be written in the form

$$U^{jk} = \epsilon^{j(0)}\delta^{jk} + \sum_{\mu\nu} V_{\mu\nu}d_{\mu\nu}{}^{jk(0)}$$
$$+ \tfrac{1}{2}\sum_{\mu\nu\kappa\lambda} V_{\mu\nu}V_{\kappa\lambda}\pi_{\mu\nu,\kappa\lambda}{}^{jk(0)}, \quad (46)$$

where it is expressed directly in the perturbations $V_{\mu\nu}$ of the charge and bond affinities.

In the case of a *real* effective Hamiltonian H_{eff}, it is convenient to introduce also the auxiliary quantities

$$\Omega_{\mu\nu}{}^j = \sum_{\alpha \neq (J)} \frac{C_{\mu}{}^{\alpha}C_{\nu}{}^{\alpha*}}{(j\alpha)} \quad (47)$$

for the evaluation of the mutabilities π and the coefficients in the eigenfunctions. According to (25), we have the symmetry relation

$$\Omega_{\mu\nu}{}^j = \sum_{\alpha \neq (J)} \frac{d_{\mu\nu}{}^{\alpha\alpha}}{(j\alpha)} = \Omega_{\nu\mu}{}^j, \quad (48)$$

and, by using (44), (26), (47), and (48), we obtain the formula

$$\pi_{\mu\nu,\kappa\lambda}{}^{jk} = \tfrac{1}{2}(d_{\mu\kappa}{}^{jk}\Omega_{\nu\lambda}{}^j + d_{\mu\lambda}{}^{jk}\Omega_{\nu\kappa}{}^j$$
$$+ d_{\nu\kappa}{}^{jk}\Omega_{\mu\lambda}{}^j + d_{\nu\lambda}{}^{jk}\Omega_{\mu\kappa}{}^j), \quad (49)$$

giving a simple way of calculating the mutabilities.

Now it remains to compute the coefficients $C_{\mu}{}^j$ used in (30) for forming the MO of the perturbed molecule. According to (36) and (41), we obtain

$$C_{\mu}{}^j = \sum_k C_{\mu}{}^{k(0)}X^{kj} = \sum_{k=(J)} C_{\mu}{}^{k(0)}X_{\text{sub}}{}^{kj}$$
$$+ \sum_{k \neq (J)} C_{\mu}{}^{k(0)}\frac{1}{(jk)}\sum_{\alpha=(J)} v^{k\alpha}X_{\text{sub}}{}^{\alpha j}. \quad (50)$$

Changing the names of the summation indices k and α in the last term, and using (42), (26), (47), and (48),

we can derive the formula

$$\begin{cases} C_{\mu}{}^j = \sum_{k=(J)} T_{\mu}{}^{k(0)}X_{\text{sub}}{}^{kj}, \\ T_{\mu}{}^{k(0)} = C_{\mu}{}^{k(0)} + \tfrac{1}{2}\sum_{\kappa\lambda} V_{\kappa\lambda}(\Omega_{\mu\kappa}{}^iC_{\lambda}{}^k + \Omega_{\mu\lambda}{}^iC_{\kappa}{}^k)^{(0)}. \end{cases} \quad (51)$$

(i) *The Nondegenerate Case.* Let us investigate in greater detail a level j which is nondegenerate in the original molecule, i.e., $m^J = 1$. According to (40), the fundamental secular equation takes the form

$$U^{jj} - \epsilon = 0, \quad (52)$$

and (46) gives then the following expression for the orbital energy in the perturbed molecule:

$$\epsilon^j = \epsilon^{j(0)} + \sum_{\mu\nu} V_{\mu\nu}d_{\mu\nu}{}^{jj} + \tfrac{1}{2}\sum_{\mu\nu\kappa\lambda} V_{\mu\nu}V_{\kappa\lambda}\pi_{\mu\nu,\kappa\lambda}{}^{jj}. \quad (53)$$

The unitary matrix X_{sub} has a single element $X_{\text{sub}}{}^{jj} = 1$, and formula (51) gives therefore for the coefficients in the perturbed MO

$$C_{\mu}{}^j = C_{\mu}{}^{j(0)} + \tfrac{1}{2}\sum_{\kappa\lambda} V_{\kappa\lambda}(\Omega_{\mu\kappa}{}^jC_{\lambda}{}^j + \Omega_{\mu\lambda}{}^jC_{\kappa}{}^j)^{(0)}. \quad (54)$$

The separate charge and bond orders may be derived from the orbital energy by using (19), and we obtain

$$q_{\mu}{}^j = q_{\mu}{}^{j(0)} + \sum_{\kappa\lambda} V_{\kappa\lambda}\pi_{\mu\mu,\kappa\lambda}{}^{jj(0)},$$
$$p_{\mu\nu}{}^j = p_{\mu\nu}{}^{j(0)} + \sum_{\kappa\lambda} V_{\kappa\lambda}\pi_{\mu\nu,\kappa\lambda}{}^{jj(0)}. \quad (55)$$

Hence it is possible to find the orbital energy, the form of the MO, and the separate charge and bond orders for the perturbed molecule, if the quantities d and π are tabulated for the original compound. By another differentiation of (55), we get

$$\pi_{\mu\mu,\kappa\kappa}{}^{jj} = \frac{\partial q_{\mu}{}^j}{\partial V_{\kappa\kappa}} = \frac{\partial^2\epsilon^j}{\partial V_{\mu\mu}\partial V_{\kappa\kappa}},$$

$$\pi_{\mu\mu,\kappa\lambda}{}^{jj} = \frac{1}{2}\frac{\partial q_{\mu}{}^j}{\partial V_{\kappa\lambda}} = \frac{\partial p_{\kappa\lambda}{}^j}{\partial V_{\mu\mu}} = \frac{1}{2}\frac{\partial^2\epsilon^j}{\partial V_{\mu\mu}\partial V_{\kappa\lambda}}, \quad (\kappa \neq \lambda), \quad (56)$$

$$\pi_{\mu\nu,\kappa\lambda}{}^{jj} = \frac{1}{2}\frac{\partial p_{\mu\nu}{}^j}{\partial V_{\kappa\lambda}} = \frac{1}{4}\frac{\partial^2\epsilon^j}{\partial V_{\mu\nu}\partial V_{\kappa\lambda}}, \quad (\mu \neq \nu, \kappa \neq \lambda),$$

showing that, for a nondegenerate level, the mutabilities are the second derivatives of the orbital energy with respect to the charge and bond affinities. Combining (17) and (56), we obtain then easily a series of connection formulas for the separate mutabilities.

(ii) *The Degenerate Case.* Let us now go back to the degenerate case with $m^J \geq 2$. In order to describe the degenerate class (J) of the unperturbed molecule, we will use a particular orthonormalized set $j', j'', j''', \cdots$ of MO belonging to (J) as a fixed reference set. The

matrices $d_{\mu\nu}{}^{jl}$ and $\pi_{\mu\nu,\kappa\lambda}{}^{jk}$ exist formally according to (26) and (44) for each pair (j, k) of orbitals of this set, but we note that these quantities cannot have any direct physical meaning, since they are not invariant against a unitary transformation of the reference system. We may consider $d_{\mu\nu}{}^{jk}$ and $\pi_{\mu\nu,\kappa\lambda}{}^{jk}$ as the first and second derivatives, respectively, of the matrix elements U^{jk}, defined by (40), with respect to the perturbation integrals, but even these relations have only formal meaning.

In this connection it is of interest to consider the transformations of the quantities $d_{\mu\nu}{}^{jk}$, $\Omega_{\mu\nu}{}^{j}$, $\pi_{\mu\nu,\kappa\lambda}{}^{jk}$, U^{jk}, etc., under a unitary transformation of the reference set, which may be of the form $\bar{C} = \mathbf{C}\mathbf{D}$, or

$$\bar{C}_\mu{}^j = \sum_{\alpha=(J)} C_\mu{}^\alpha D^{\alpha j}, \tag{57}$$

where $\mathbf{D}$ is an arbitrary unitary matrix of order m^J:

$$\mathbf{D}^\dagger\mathbf{D} = \mathbf{D}\mathbf{D}^\dagger = 1. \tag{58}$$

Combining (26) and (57), we obtain

$$d_{\mu\nu}{}^{jk} = \sum_{\alpha,\beta=(J)} D^{\dagger j\alpha} d_{\mu\nu}{}^{\alpha\beta} D^{\beta k}. \tag{59}$$

For the total quantities (21), obtained by summing once over the contributions from all indices j', j'', j''', $\cdots$ associated with the class (J), we get

$$d_{\mu\nu}{}^{JJ} = \sum_{j=(J)} d_{\mu\nu}{}^{jj} = \sum_{\alpha,\beta=(J)} d_{\mu\nu}{}^{\alpha\beta} \sum_{j=(J)} D^{\beta j} D^{\dagger j\alpha}$$

$$= \sum_{\alpha,\beta=(J)} d_{\mu\nu}{}^{\alpha\beta}\delta^{\alpha\beta} = \sum_{\alpha=(J)} d_{\mu\nu}{}^{\alpha\alpha} = d_{\mu\nu}{}^{JJ}, \tag{60}$$

where we have utilized the unitary property (58) of $\mathbf{D}$. This gives a detailed proof of the invariance theorem stated in connection with (21).

In forming the quantities $\Omega_{\mu\nu}{}^{j}$ by means of (48), we sum only over complete classes of eventually degenerate levels, and according to (60), they are therefore invariant:

$$\Omega_{\mu\nu}{}^{j,\mathrm{tr}} = \Omega_{\mu\nu}{}^{j}, \tag{61}$$

and they are further the same for all indices j belonging to the same degenerate class. By using (49), (59), and (61), we get for the mutabilities

$$\bar{\pi}_{\mu\nu,\kappa\lambda}{}^{jk} = \sum_{\alpha,\beta=(J)} D^{\dagger j\alpha} \pi_{\mu\nu,\kappa\lambda}{}^{\alpha\beta} D^{\beta k}. \tag{62}$$

If we define the *total mutabilities* of the class (J) by by summing once over all indices j', j'', j''', $\cdots$:

$$\pi_{\mu\nu,\kappa\lambda}{}^{JJ} = \sum_{j=(J)} \pi_{\mu\nu,\kappa\lambda}{}^{jj}, \tag{63}$$

we obtain again a quantity which can be shown to be invariant in the same way as (60). All these quantities are, of course, associated with the unperturbed molecule, but, for the sake of simplicity, we have omitted the upper index zero.

Let us now consider the quantities in the perturbation scheme. According to (59) and (62), the elements U^{jk} of the fundamental matrix (46) have the transformation property

$$\bar{U}^{jk} = \sum_{\alpha,\beta=(J)} D^{\dagger j\alpha} U^{\alpha\beta} D^{\beta k}. \tag{64}$$

Hence, the matrix $\bar{U}$ undergoes only a unitary transformation, which implies that its eigenvalues are invariant. According to (60), the sum of the diagonal elements of $\bar{U}$ is another invariant.

Let us assume that the degeneracy is completely removed by the perturbation under consideration. If $\mathbf{X}_{\mathrm{sub}}$ and $\bar{X}_{\mathrm{sub}}$ are the unitary matrices of order m^J which transform $\mathbf{U}$ and $\bar{U}$, respectively, to diagonal form, then we have the relation

$$\bar{X}_{\mathrm{sub}} = \mathbf{D}^\dagger\mathbf{X}, \tag{65}$$

for we have the matrix equations

$$\bar{X}_{\mathrm{sub}}{}^\dagger \bar{U} \bar{X}_{\mathrm{sub}} = \mathbf{X}_{\mathrm{sub}}{}^\dagger \mathbf{D} \cdot \mathbf{D}^\dagger \mathbf{U} \mathbf{D} \cdot \mathbf{D}^\dagger \mathbf{X}_{\mathrm{sub}}$$
$$= \mathbf{X}_{\mathrm{sub}}{}^\dagger \mathbf{U} \mathbf{X}_{\mathrm{sub}} = \text{diagonal matrix.} \tag{66}$$

The matrix $\mathbf{T}$, defined by (51), has the transformation property $\bar{T} = \mathbf{T}\mathbf{D}$. Using this relation and (65), we find that also the coefficients of the perturbed MO given by (51) are invariant, for

$$\bar{C} = \bar{T}\bar{X}_{\mathrm{sub}} = \mathbf{T}\mathbf{D} \cdot \mathbf{D}^\dagger\mathbf{X}_{\mathrm{sub}} = \mathbf{T}\mathbf{X}_{\mathrm{sub}} = \mathbf{C}. \tag{67}$$

This means that the eigenvalues and the eigenfunctions are completely independent of the particular choice of reference set used for describing the degenerate class of the unperturbed molecule.

If the degenerate class (J) is split up in the perturbed molecule, we can determine the separate charge and bond orders of the perturbed orbitals according to (51) and the definitions (15), but, in such a case, the algebraic equation (40) has first to be solved.

There is one information about the perturbed molecule which can be obtained without solving (40) explicitly, namely the properties of the total quantities associated with the class (J) as a whole. By applying the coefficient theorem for the sum of the roots of an algebraic equation to (40), and by using (60) and (63), we get

$$\epsilon^J = \sum_{j=(J)} \epsilon^j = \sum_{j=(J)} U^{jj} = m^j \epsilon^{J(0)}$$

$$+ \sum_{\mu\nu} V_{\mu\nu} d_{\mu\nu}{}^{JJ(0)} + \frac{1}{2} \sum_{\mu\nu,\kappa\lambda} V_{\mu\nu} V_{\kappa\lambda} \pi_{\mu\nu,\kappa\lambda}{}^{JJ(0)}, \tag{68}$$

a result which is independent of the splitting of the class (J). Hence we obtain for the *total charge and bond orders* associated with the class (J) in the perturbed molecule

$$q_\mu{}^J = \frac{\partial\epsilon^J}{\partial V_{\mu\mu}} = q_\mu{}^{J(0)} + \sum_{\kappa\lambda} V_{\kappa\lambda}\pi_{\mu\mu,\kappa\lambda}{}^{JJ(0)},$$

$$p_{\mu\nu}{}^J = \frac{1}{2}\frac{\partial\epsilon^J}{\partial V_{\mu\nu}} = p_{\mu\nu}{}^{J(0)} + \sum_{\kappa\lambda} V_{\kappa\lambda}\pi_{\mu\nu,\kappa\lambda}{}^{JJ(0)}, \quad (\mu\neq\nu), \tag{69}$$

TABLE I.

Notation used here	Notation used by Coulson and Longuet-Higgins	
$\pi_{\mu\mu,\,\kappa\kappa}^{\text{tot}}$	$\pi_{\mu,\,\kappa}$	
$\pi_{\mu\mu,\,\kappa\lambda}^{\text{tot}}$	$\pi_{\kappa\lambda,\,\mu} = \tfrac{1}{2}\pi_{\mu,\,\kappa\lambda}$	$(\kappa \neq \lambda)$
$\pi_{\mu\nu,\,\kappa\lambda}^{\text{tot}}$	$\tfrac{1}{2}\pi_{\mu\nu,\,\kappa\lambda}$	$(\mu \neq \nu,\ \kappa \neq \lambda)$

showing that the total mutabilities $\pi_{\mu\nu,\,\kappa\lambda}^{JJ(0)}$ may be considered as the second derivatives of the sum ϵ^J of the orbital energies of class (J), with respect to the perturbation integrals $V_{\mu\nu}$.

In this connection, we may also say a few words about the total quantities associated with a complex of electrons, obtained by summing over all occupied orbitals:

$$\epsilon^{\text{tot}} = \sum_j \epsilon^j, \quad q_\mu^{\text{tot}} = \sum_j q_\mu^j, \quad p_{\mu\nu}^{\text{tot}} = \sum_j p_{\mu\nu}^j,$$

$$d_{\mu\nu}^{\text{tot}} = \sum_j d_{\mu\nu}^{jj}, \quad \pi_{\mu\nu,\,\kappa\lambda}^{\text{tot}} = \sum_j \pi_{\mu\nu,\,\kappa\lambda}^{jj}. \tag{70}$$

By summing over all classes involved in the system, we obtain from (68) and (70),

$$\epsilon^{\text{tot}} = \epsilon^{\text{tot}(0)} + \sum_{\mu\nu} V_{\mu\nu} d_{\mu\nu}^{\text{tot}(0)} + \tfrac{1}{2}\sum_{\mu\nu\kappa\lambda} V_{\mu\nu} V_{\kappa\lambda} \pi_{\mu\nu,\,\kappa\lambda}^{\text{tot}(0)}. \tag{71}$$

For the total charge and bond orders, we get further

$$q_\mu^{\text{tot}} = \frac{\partial \epsilon^{\text{tot}}}{\partial V_{\mu\mu}} = q_\mu^{\text{tot}(0)} + \sum_{\kappa\lambda} V_{\kappa\lambda} \pi_{\mu\mu,\,\kappa\lambda}^{\text{tot}(0)},$$

$$p_{\mu\nu}^{\text{tot}} = \frac{1}{2}\frac{\partial \epsilon^{\text{tot}}}{\partial V_{\mu\nu}} = p_{\mu\nu}^{\text{tot}(0)} + \sum_{\kappa\lambda} V_{\kappa\lambda} \pi_{\mu\nu,\,\kappa\lambda}^{\text{tot}(0)}, \tag{72}$$

and, for the total mutabilities, we finally obtain

$$\pi_{\mu\mu,\,\kappa\kappa}^{\text{tot}} = \frac{\partial q_\mu^{\text{tot}}}{\partial V_{\kappa\kappa}} = \frac{\partial^2 \epsilon^{\text{tot}}}{\partial V_{\mu\mu} \partial V_{\kappa\kappa}},$$

$$\pi_{\mu\mu,\,\kappa\lambda}^{\text{tot}} = \frac{1}{2}\frac{\partial q_\mu^{\text{tot}}}{\partial V_{\kappa\lambda}} = \frac{\partial p_{\kappa\lambda}^{\text{tot}}}{\partial V_{\mu\mu}} = \frac{1}{2}\frac{\partial^2 \epsilon^{\text{tot}}}{\partial V_{\mu\mu} \partial V_{\kappa\lambda}}, \quad (\kappa \neq \lambda) \tag{73}$$

$$\pi_{\mu\nu,\,\kappa\lambda}^{\text{tot}} = \frac{1}{2}\frac{\partial p_{\mu\nu}^{\text{tot}}}{\partial V_{\kappa\lambda}} = \frac{1}{4}\frac{\partial^2 \epsilon^{\text{tot}}}{\partial V_{\mu\nu} \partial V_{\kappa\lambda}}, \quad (\mu \neq \nu,\ \kappa \neq \lambda).$$

All these total quantities have previously been investigated by Coulson and Longuet-Higgins,[5] who introduced the name *mutual polarizabilities* for the derivatives of the charge and bond orders. Since this term is used in another meaning also in the theory of dielectrics, we have here instead used the name *mutabilities* proposed by Lennard-Jones.[4] We note that, in order to maintain the symmetry relations (45), which for the total quantities take the form

$$\pi_{\mu\nu,\,\kappa\lambda}^{\text{tot}} = \pi_{\nu\mu,\,\kappa\lambda}^{\text{tot}}, \quad \pi_{\mu\nu,\,\kappa\lambda}^{\text{tot}} = \pi_{\kappa\lambda,\,\mu\nu}^{\text{tot}}, \tag{74}$$

and which are of essential importance for the simplicity of our formulas, we have changed also the notations slightly. Consequently, for quantities $\pi_{\mu\nu,\,\kappa\lambda}$ having the last pair of indices corresponding to a bond, a factor $\tfrac{1}{2}$ in the treatment in reference 5 is here included in the symbol itself; see also Table I for comparison.

Treatment of a Doubly Degenerate Level

The solution of the secular equation (40) is simple in the case of a doubly degenerate level, $m^J = 2$, and, since this type of degeneracy is also of particular importance in the theory of conjugated systems, we will treat it in somewhat greater detail here. This example may be instructive for the study of the higher degeneracies, too.

(a) *Real reference set.* We may use either a real or a complex description of the degenerate class (J), and we will begin with the real case. The matrix U^{jk}, defined by (39), is Hermitean, $U^{ki} = U^{ik*}$, and, for a purely real representation, it is therefore also symmetric:

$$U^{ki} = U^{ik}. \tag{75}$$

For the sake of simplicity, let us denote the reference orbitals of the class by the upper indices 1 and 2. The submatrix U associated with the class has the form

$$\mathbf{U}_{\text{sub}} = \begin{pmatrix} U^{11} & U^{12} \\ U^{21} & U^{22} \end{pmatrix}, \tag{76}$$

and, according to (40), its eigenvalues are given by

$$\epsilon = \tfrac{1}{2}\{(U^{11} + U^{22}) \pm [(U^{11} - U^{22})^2 + 4U^{12}U^{21}]^{\frac{1}{2}}\}. \tag{77}$$

The unitary matrix $\mathbf{X}$, which transforms $\mathbf{U}$ to diagonal form, is found by solving the equation system $\mathbf{UX} = \mathbf{X}\epsilon$ for the known eigenvalues. By introducing the angle φ given by

$$\text{tg}\,\varphi = \frac{(U^{11} - U^{22}) - [(U^{11} - U^{22})^2 + 4U^{12}U^{21}]^{\frac{1}{2}}}{2U^{12}}, \tag{78}$$

the solution may be expressed in the form

$$\mathbf{X}_{\text{sub}} = \begin{pmatrix} \cos\varphi & \sin\varphi \\ -\sin\varphi & \cos\varphi \end{pmatrix}, \tag{79}$$

and the coefficients C_μ^j of the perturbed MO can then be calculated according to (51). A still simpler formula for φ is given below.

(b) *Complex reference set.* We shall discuss a complex description of the doubly degenerate class, which is so chosen that the two reference orbitals for the unperturbed molecule are *conjugate complex* functions. By using this property and the ordinary definitions, it is easily shown that the charge orders, the bond orders, and the mutabilities for $j = k$ are the same for both unperturbed orbitals. Since the diagonal elements of the matrix $\bar{U}_{\text{sub}}$ for the perturbed molecule are also the

same, the eigenvalues of $\bar{U}_{sub}$ are now given by

$$\epsilon = \bar{U}^{11} \pm |\bar{U}^{12}|. \tag{80}$$

If the angle φ is defined as half the argument of the complex quantity U^{12}, the matrix $\bar{U}_{sub}$ is further transformed to diagonal form by the unitary matrix

$$\bar{X}_{sub} = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{i\varphi} & -ie^{i\varphi} \\ e^{-i\varphi} & ie^{-i\varphi} \end{pmatrix}, \tag{81}$$

and the coefficients $C_\mu{}^j$ of the perturbed MO can then be calculated according to (51).

Finally, we will investigate the connection between the real and complex descriptions. For the unperturbed molecule, our complex conjugate reference set may be obtained from an arbitrary real set by a unitary transformation (57) with the transformation matrix

$$\mathbf{D} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix}. \tag{82}$$

According to (64), we then obtain $\bar{U}_{sub} = \mathbf{D}^\dagger \mathbf{U}_{sub} \mathbf{D}$, or

$$\bar{U}_{sub} = \begin{pmatrix} \bar{U}^{11} & \bar{U}^{12} \\ \bar{U}^{21} & \bar{U}^{22} \end{pmatrix}$$
$$= \frac{1}{2} \begin{pmatrix} U^{11} + U^{22}; & U^{11} - U^{22} - 2iU^{12} \\ U^{11} - U^{22} + 2iU^{12}; & U^{11} + U^{22} \end{pmatrix}. \tag{83}$$

A comparison between (77) and (80) based on (83) shows at once that the eigenvalues are the same. The angle φ is in the complex case defined by

$$\operatorname{tg} 2\varphi = I\{U^{12}\}/Re\{U^{12}\} = -2U^{12}/(U^{11} - U^{22}), \tag{84}$$

which implies that it is identical with the angle φ in the real case, since (84) can be derived from (78). Finally, for the matrix (81), we have $\bar{X}_{sub} = \mathbf{D}^\dagger X_{sub}$ in agreement with (65).

4. Hybridization between Atomic Orbitals of 2s and 2p Types

The MO-LCAO theory of molecules is essentially based on the assumption that it is possible to make a convenient choice of atomic orbitals for the atoms constituting the molecule under consideration, and we will therefore discuss this problem in greater detail. In investigating the simplest conjugated compounds we are particularly interested in the AO of the atoms of the elements belonging to the second row of the periodic system. In the ground state of these elements, the two electrons occupying the 1s-orbital do not take part in bond formation, so we have to consider only the outer electrons distributed over the four orbitals 2s, $2px$, $2py$, and $2pz$, having about the same energy. These AO are given by the formulas

$$\phi_{2s} = \frac{1}{(4\pi)^{\frac{1}{2}}} \frac{f_{2s}(r)}{r}, \qquad \phi_{2px} = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \frac{f_{2p}(r)}{r^2} x,$$
$$\phi_{2py} = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \frac{f_{2p}(r)}{r^2} y, \qquad \phi_{2pz} = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \frac{f_{2p}(r)}{r^2} z, \tag{85}$$

where $f_{2s}(r)$ and $f_{2p}(r)$ are the radial wave functions, which may be of Slater or Hartree-Fock type. The p-orbitals are direction dependent, and we introduce the notation $2p\xi$ for a $2p$-orbital in the direction of the ξ-axis, where ξ also may be the distance to a plane through the origin perpendicular to this axis. If the quantities $\cos\gamma_{\xi x}$, $\cos\gamma_{\xi y}$, and $\cos\gamma_{\xi z}$ are the direction cosines for the ξ-axis, then we have

$$\phi_{2p\xi} = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \frac{f_{2p}(r)}{r^2} \xi,$$
$$\xi = x\cos\gamma_{\xi x} + y\cos\gamma_{\xi y} + z\cos\gamma_{\xi z}. \tag{86}$$

Such a $2p\xi$-orbital is antisymmetric with respect to the plane $\xi = 0$, and it has therefore the same extension along the positive and negative directions of the ξ-axis.

As was first pointed out by Pauling[23] and Slater,[24] an orbital of the form

$$h = a\phi_{2s} + (1 - a^2)^{\frac{1}{2}} \cdot \phi_{2p\xi}, \tag{87}$$

with $a > 0$, has its largest extension in the direction of the ξ-axis, and it may therefore be convenient for the description of a *directed valency*. The mixing of s- and p-orbitals is called a hybridization, and the orbital h in (87) is called a *hybrid* with its direction along the positive ξ-axis.

The theory of hybridization has been treated by several authors,[25] and here we only wish to stress the simplicity of the mathematics involved, if the theory is presented in matrix form. From the four AO given by (85), we can by linear combinations form four linearly independent hybrids h_1, h_2, h_3, and h_4, and we may write the hybridization in the form $\mathbf{h} = \boldsymbol{\phi}\mathbf{Y}$, or

$$h_k = \sum_\alpha \phi_\alpha Y_{\alpha k}, \tag{88}$$

where the transformation matrix has the form

$$\mathbf{Y} = \begin{bmatrix} a_1 & a_2 & a_3 & a_4 \\ a_{x1} & a_{x2} & a_{x3} & a_{x4} \\ a_{y1} & a_{y2} & a_{y3} & a_{y4} \\ a_{z1} & a_{z2} & a_{z3} & a_{z4} \end{bmatrix}. \tag{89}$$

Here we restrict $\mathbf{Y}$ to having only real elements. The quantity $a_k{}^2$ gives the amount of s-character in the

[23] L. Pauling, Proc. Nat. Acad. Sci. U. S. 14, 359 (1928); J. Am. Chem. Soc. 53, 1367 (1931).
[24] J. C. Slater, Phys. Rev. 37, 481 (1931).
[25] See, for instance, C. A. Coulson, Proc. Roy. Soc. (Edinburgh) 61, 115 (1941).

hybrid h_k. According to Pauling,[26] the approximate bond strength of the hybrid h_k is given by the expression $a_k + (3 - 3a_k^2)^{\frac{1}{2}}$, but we are not going to use this property here. The given set (85) is orthonormalized, and, if we impose on the hybrids the fundamental condition that they should be orthonormalized, too, the hybridization matrix $\mathbf{Y}$ must be a unitary matrix, $\mathbf{Y}^\dagger \mathbf{Y} = \mathbf{Y}\mathbf{Y}^\dagger = 1$, or

$$\sum_\alpha Y_{\alpha k} Y_{\alpha l} = \sum_\alpha Y_{k\alpha} Y_{l\alpha} = \delta_{kl}. \qquad (90)$$

A comparison between Eqs. (86)–(89) shows further that the largest extension of the hybrid h_k is along a k-axis having the direction cosines

$$\cos\gamma_{xk} = \frac{a_{xk}}{(1 - a_k^2)^{\frac{1}{2}}}, \quad \cos\gamma_{yk} = \frac{a_{yk}}{(1 - a_k^2)^{\frac{1}{2}}},$$

$$\cos\gamma_{zk} = \frac{a_{zk}}{(1 - a_k^2)^{\frac{1}{2}}}. \qquad (91)$$

By using this relation and the orthogonality condition $a_{xk}a_{xl} + a_{yk}a_{yl} + a_{zk}a_{zl} = -a_k a_l$, contained in (90), we can then derive the following basic formula for the angle γ_{kl} between the axes of two hybrids, h_k and h_l:

$$\alpha_{kl} = \cos\gamma_{kl} = -\frac{a_k a_l}{\{(1 - a_k^2)(1 - a_l^2)\}^{\frac{1}{2}}}. \qquad (92)$$

The general problem of the evaluation of the appropriate matrix $\mathbf{Y}$ for a particular atom in a molecule is very important, but the principle of "maximum overlapping," stated by Pauling and by Slater for this purpose, has not yet been fully theoretically proven.[27] Recently, Mulliken[28] has investigated the connection between the overlap integrals and the amounts of s-character of the bonding hybrids in a diatomic molecule, but the corresponding bond energies are still treated only by means of a semi-empirical formula.

We note that the simple formula (92) will sometimes give useful informations about the form of the matrix $\mathbf{Y}$, for instance, when the amounts of s-character of the four hybrids h_k have been found in some other way. By using the four quantities a_1, a_2, a_3, a_4, fulfilling the condition $\sum a_k^2 = 1$ contained in (90), formula (92) gives the angles between the axes of the hybrids. Utilizing these angles for fixing four axes in the space, determined except for a rigid rotation, we can then evaluate the remaining part of the elements of $\mathbf{Y}$ from the known

[26] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), p. 85.
[27] Compare A. Maccoll, Trans. Faraday Soc. 46, 359 (1950) and W. Moffitt, Proc. Roy. Soc. (London) A202, 534, 548 (1950).
[28] R. S. Mulliken, J. Chem. Phys. 19, 900 (1951); R. S. Mulliken, J. Am. Chem. Soc. 72, 4493 (1950).

direction cosines by using (91):

$$a_{xk} = (1 - a_k^2)^{\frac{1}{2}} \cos\gamma_{xk}, \quad a_{yk} = (1 - a_k^2)^{\frac{1}{2}} \cos\gamma_{yk},$$

$$a_{zk} = (1 - a_k^2)^{\frac{1}{2}} \cos\gamma_{zk}. \qquad (93)$$

This gives a very simple method for constructing, e.g., the conventional matrices $\mathbf{Y}$ for the basic digonal, trigonal, and tetragonal hybridizations[25] associated with the following sets of s-coefficients: $a_k = (1/2^{\frac{1}{2}}, 1/2^{\frac{1}{2}}, 0, 0)$, $a_k = (1/3^{\frac{1}{2}}, 1/3^{\frac{1}{2}}, 1/3^{\frac{1}{2}}, 0)$, and $a_k = (1/2, 1/2, 1/2, 1/2)$, respectively.

We note that also the reverse process may be useful, i.e., the calculation of the amount of s-character and the construction of the explicit forms of the hybrids from, for instance, experimentally known bond angles. For this purpose, let us introduce a quantity κ_k, the *characteristic s-number* of the hybrid h_k, by

$$\kappa_k = \frac{a_k}{(1 - a_k^2)^{\frac{1}{2}}}, \quad a_k = \frac{\kappa_k}{(1 + \kappa_k^2)^{\frac{1}{2}}}. \qquad (94)$$

The basic formula (92) may then be written in the form

$$\alpha_{kl} = - \kappa_k \kappa_l. \qquad (95)$$

Because of the product form and the condition $\sum a_k^2 = \sum \kappa_k^2/(1 + \kappa_k)^2 = 1$, only *three* of the six elements α_{kl} are independent in the general case. Let us first consider the case that the directions of the three hybrids h_1, h_2, and h_3 are known, and that the angles between them all are *different* from 90°. The characteristic s-numbers κ_1, κ_2, κ_3 can then be determined from the three known direction cosines α_{12}, α_{23}, α_{31}, according to (95), which gives

$$\omega = (-\alpha_{12}\alpha_{23}\alpha_{31})^{\frac{1}{2}},$$

$$\kappa_1 = -\frac{\omega}{\alpha_{23}}, \quad \kappa_2 = -\frac{\omega}{\alpha_{31}}, \quad \kappa_3 = -\frac{\omega}{\alpha_{12}}. \qquad (96)$$

The coefficients a_1, a_2, and a_3 are then found from (94), and a_4 is computed from the condition $\sum a_k^2 = 1$. Finally the other elements of $\mathbf{Y}$ are calculated according to (93).

As an example of this procedure, we shall discuss the molecules in which we are particularly interested here, namely the *conjugated systems*, i.e., the organic compounds having alternating single and double bonds in the conventional structure formulas. By using x-ray and electron diffraction technique, one has found experimentally that the conjugated systems are almost completely coplanar and that the bond angles in the plane are 120°. This indicates strongly that the bonds associated with these "trivalent" carbon atoms or their equivalents are formed by three coplanar hybrids h_1, h_2, and h_3 with the angles 120° between them, whereas the

type of the fourth hybrid is not known from the beginning.

However, utilizing the three angles of 120° and formulas (96) and (94), we obtain:

$$\alpha_{12} = \alpha_{23} = \alpha_{31} = \cos 120° = -\tfrac{1}{2}, \quad \omega = 1/2\sqrt{2},$$

$$\kappa_1 = \kappa_2 = \kappa_3 = 1/\sqrt{2}, \tag{97}$$

$$a_1 = a_2 = a_3 = 1/\sqrt{3}; \quad a_4 = 0.$$

If our basic assumption of the orthonormality of the hybrids is true, the fourth orbital h_4 must therefore be a pure $2p$-orbital which is perpendicular to the (h_1, h_2, h_3)-plane.

Let us put our coordinate system with the xy-plane in the molecular plane of the conjugated system. The three hybrids in this plane are usually called σ-orbitals and are denoted by σ_1, σ_2, σ_3, and the fourth hybrid is called a π-orbital. By fixing the directions of these orbitals according to Fig. 1 and by using (93), we obtain for the matrix $\mathbf{Y}$:

$$\mathbf{Y} = \begin{pmatrix} \dfrac{1}{\sqrt{3}} & \dfrac{1}{\sqrt{3}} & \dfrac{i}{\sqrt{3}} & 0 \\[2mm] \sqrt{2}/\sqrt{3} & -\dfrac{1}{(6)^{\frac{1}{2}}} & -\dfrac{1}{(6)^{\frac{1}{2}}} & 0 \\[2mm] 0 & \dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} & 0 \\[2mm] 0 & 0 & 0 & 1 \end{pmatrix}. \tag{98}$$

Of the four outer electrons of a normal carbon atom in the "trivalent" state, three electrons are placed in the orbitals σ_1, σ_2, and σ_3, forming *single bonds* together with other similar electrons with opposite spin from the neighboring atoms, and the fourth electron is placed in the π-orbital contributing to a *partial double bond* according to the MO-theory. Here we are particularly interested in these π-electrons.

In the MO–LCAO theory developed in this paper, we have up till now taken *all* bonding electrons into account in forming the matrices $\mathbf{S}$, $\mathbf{H}$, and $\mathbf{H}'$ for the molecule under consideration. However, the σ-orbitals and the π-orbitals are of a different symmetry type, since the former are symmetric and the latter antisymmetric with respect to the molecular plane. For the overlap matrix $S_{\mu\nu}$ as well as for the energy matrix $H_{\mu\nu}$ and $H_{\mu\nu}'$, based on a Hartree-Fock-Dirac effective Hamiltonian for the ground state, this implies that all *mixed* elements with $(\mu\nu) = (\pi\sigma)$ will vanish identically. All these matrices will therefore exactly split into a
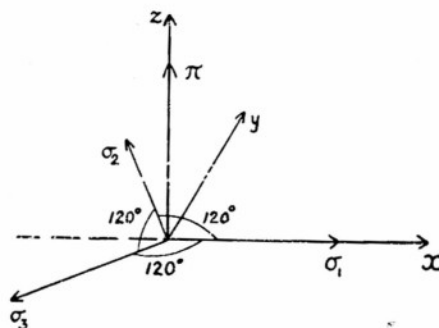

Fig. 1. Trigonal hybridization in a conjugated system.

π-part and a σ-part:

$$\mathbf{S} = \begin{pmatrix} \mathbf{S}_\pi & 0 \\ 0 & \mathbf{S}_\sigma \end{pmatrix}, \quad \mathbf{H} = \begin{pmatrix} \mathbf{H}_\pi & 0 \\ 0 & \mathbf{H}_\sigma \end{pmatrix},$$

$$\mathbf{H}' = \begin{pmatrix} \mathbf{H}_\pi' & 0 \\ 0 & \mathbf{H}_\sigma' \end{pmatrix}. \tag{99}$$

This result does not mean that the treatment of the π-electrons can be entirely separated from the treatment of the σ-electrons since both types are involved in the mathematical expression for the effective Hamiltonian causing a rather complicated interaction of the Coulomb and the exchange type. However, if the elements of $\mathbf{H}'$ in some way have been evaluated, then the questions of finding the eigenvalues and the eigenfunctions of $\mathbf{H}_\pi'$ and $\mathbf{H}_\sigma'$ may be considered as independent problems. A more detailed study of the possibility of separating the treatments of the π- and σ-electrons has recently been given by Altmann.[29]

Before concluding this section, we will go back to the general hybridization problem, where it remains to investigate the special case when the three hybrids h_1, h_2, and h_3 with known directions form angles, of which at least one is 90°. In this case the solution (96) breaks down, and the problem must be reexamined.

Let us consider the case of $\alpha_{12} = 0$. According to (95), at least one of the relations $\alpha_{13} = 0$ or $\alpha_{23} = 0$ must hold, and if, e.g., the former is true, we conclude that $\kappa_1 = 0$ i.e., that the hybrid h_1 is a pure $2p$-orbital, and that the remaining orbitals h_2, h_3, and h_4 all have their directions in the plane perpendicular to h_1. More information is then needed for solving the problem, and we will therefore consider the triple α_{23}, α_{34}, and α_{42}, which usually determines the values of κ_2, κ_3, and κ_4, in a way analogous to (96). However, also this solution breaks down if, e.g., $\alpha_{23} = 0$. In this case, at least one of the relations $\alpha_{24} = 0$ or $\alpha_{34} = 0$ must be true, and if the former holds, we conclude that $\kappa_2 = 0$, i.e., that h_2 is a pure $2p$-orbital, and that the remaining orbitals h_3 and h_4 must have their directions along the line perpendicu-

[29] S. L. Altmann, Proc. Roy. Soc. (London) A210, 327, 343 (1952). See also Coulson, March, and Altman, Proc. Nat. Acad. Sci. U. S. 38, 372 (1952).
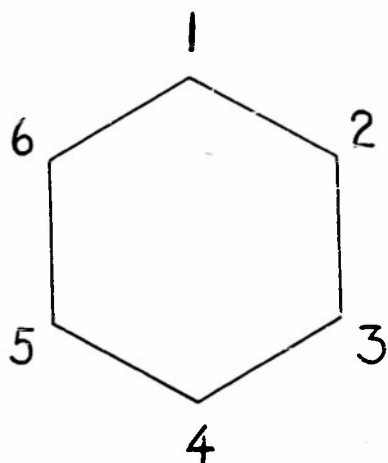
FIG. 2. Numbering of the carbon atoms in a benzene ring.

lar to the (h_1, h_2)-plane. We observe that it is impossible to determine the amount of s-character in these orbitals from the angular dependence, but that we have $a_3^2 + a_4^2 = 1$. The acetylene molecule C_2H_2 is an example of a hybridization of this type.

PART II. APPLICATIONS OF THE MOLECULAR ORBITAL THEORY TO THE PERTURBED BENZENE RING

5. Properties of the π-Orbitals of the Unperturbed Benzene Molecule

Here we will apply the MO-theory developed in Part I to the treatment of the benzene molecule, C_6H_6, which represents the simplest example of a conjugated system of the ring type. According to the general theorem proven in the previous section in connection with the formula (99), the fundamental matrices $\mathbf{S}$, $\mathbf{H}$, and $\mathbf{H}'$ for all bonding electrons exactly split into two parts, a π-part and a σ-part. In this paper we are going to discuss only the former, i.e., the matrices $\mathbf{S}_\pi$, $\mathbf{H}_\pi$, and $\mathbf{H}_\pi'$ of order six, which are associated with the six π-orbitals of the ring. We will number the atoms and the π-AO according to Fig. 2.

The benzene problem is essentially simplified by the high symmetry D_{6h} of the molecule. The π-problem may be considered as having a special form of cyclic symmetry of order N, for $N=6$.[30] Treating first the general case, a matrix $\mathbf{A}$ is said to be a cyclic matrix of order N, if it fulfills the conditions

$$A_{\mu,\nu} = A_{0,\nu-\mu} = A_p, \quad (p=\nu-\mu); \quad A_{p+N} = A_N. \quad (100)$$

Such a matrix is a linear form of the more general crystal matrix, and it is easily proven[31] that the matrix $\mathbf{A}$ is transformed into diagonal form by the unitary matrix

$$C_\mu^i = \frac{1}{N^{\frac{1}{2}}} e^{2\pi i \mu j/N}, \quad j=0, 1, \cdots, N-1. \quad (101)$$

[30] The case of $N=3$ occurs, for example, in a treatment of borazole by C. C. J. Roothaan and R. S. Mulliken, J. Chem. Phys. 16, 118 (1948).
[31] See F. Bloch, Z. Physik 52, 555 (1929).

The eigenvalues of $\mathbf{A}$ are the diagonal elements of the matrix $\mathbf{a} = \mathbf{C}^\dagger \mathbf{A} \mathbf{C}$:

$$a^i = (\mathbf{C}^\dagger \mathbf{A} \mathbf{C})^{ii} = \sum_{p=0}^{N-1} A_p \exp(2\pi i p j/N). \quad (102)$$

By using the same unitary transformation, it is also easy to calculate any matrix $\mathbf{F}$, which is a function of $\mathbf{A}$, $\mathbf{F} = F(\mathbf{A})$, for we obtain

$$\mathbf{F} = \mathbf{C} F(\mathbf{C}^\dagger \mathbf{A} \mathbf{C}) \mathbf{C}^\dagger = \mathbf{C} F(\mathbf{a}) \mathbf{C}^\dagger, \quad (103)$$

and

$$\mathbf{F}_{\mu\nu} = \frac{1}{N} \sum_{j=0}^{N-1} F(a^i) \exp\{2\pi i (\mu-\nu) j/N\}. \quad (104)$$

The product of two cyclic matrices, $\mathbf{A}$ and $\mathbf{B}$, of order N is further another cyclic matrix of the same order, and we have

$$(\mathbf{AB})_p = \sum_{\alpha=0}^{N-1} A_\alpha B_{p-\alpha}. \quad (105)$$

Let us now consider the case of the π-electrons of benzene, i.e., $N=6$. The fundamental matrices $\mathbf{H}$ and $\mathbf{S}$ are both cyclic matrices of order 6, and we introduce the customary notations:

$$H_{\mu\nu} = (\alpha, \beta_1, \beta_2, \beta_3, \beta_2, \beta_1)_{\text{cyclic}},$$
$$S_{\mu\nu} = (0, S_1, S_2, S_3, S_2, S_1)_{\text{cyclic}}. \quad (106)$$

By using (105), it is easily shown that the matrices $\mathbf{S}$ and $\mathbf{H}$ commute, $\mathbf{SH} = \mathbf{HS}$, and the matrix $\mathbf{H}'$ given by (7) is therefore simplified to the form

$$\mathbf{H}' = \mathbf{H}(1+\mathbf{S})^{-1}. \quad (107)$$

Since $\mathbf{H}'$ is another cyclic matrix of order 6, it is also transformed to diagonal form by the unitary transformation (101) with $N=6$, and we obtain the orbital energies

$$\epsilon^i = \frac{\alpha + 2\beta_1 \cos\pi j/3 + 2\beta_2 \cos 2\pi j/3 + \beta_3 \cos\pi j}{1 + 2S_1 \cos\pi j/3 + 2S_2 \cos 2\pi j/3 + S_3 \cos\pi j}, \quad (108)$$

where $j=0, 1, \cdots 5$, or $j=0, \pm1, \pm2, 3$. We note that the levels $j=0$ and $j=3$ are nondegenerate, whereas the levels $j=\pm1$ and $j=\pm2$ are doubly degenerate. By using the diagonal matrix $\mathbf{s} = \mathbf{C}^\dagger \mathbf{S} \mathbf{C}$ with elements given by (102), formula (108) is easily derived from (107) by means of the matrix relation

$$\mathbf{C}^\dagger \mathbf{H}' \mathbf{C} = \mathbf{C}^\dagger \mathbf{H} (1+\mathbf{S})^{-1} \mathbf{C} = \mathbf{C}^\dagger \mathbf{H} \mathbf{C} \cdot (1+\mathbf{s})^{-1}. \quad (109)$$

Introducing the quantities $\gamma_k = \beta_k - \alpha S_k$ $(k=1, 2, 3)$, which are invariant[32] against an arbitrary change of the zero-point of the effective Hamiltonian, we can finally write the orbital energies in the form

$$\epsilon^i = \alpha + (2\gamma_1 \cos\pi j/3 + 2\gamma_2 \cos 2\pi j/3 + \gamma_3 \cos\pi j)/(1+s_j). \quad (110)$$

[32] P. O. Löwdin, J. Chem. Phys. 18, 365 (1950); see p. 368.

According to (101) for $N = 6$, the coefficients C in the molecular orbitals are given by

$$C_\mu{}^i = \frac{1}{6^{\frac{1}{2}}} e^{\pi i \mu j/3}, \tag{111}$$

and the MO themselves have therefore the form

$$\psi^i = \frac{1}{6^{\frac{1}{2}}} \sum_{\mu=1}^{6} \varphi_\mu e^{\pi i \mu j/3}, \tag{112}$$

where φ_μ are the orthonormalized π-AO. By using the matrix relation

$$\psi = \varphi C = \phi(1+S)^{-\frac{1}{2}} C = \phi C(1+s)^{-\frac{1}{2}}, \tag{113}$$

the MO can also be expressed in the form

$$\psi^i = (6 + 6s^i)^{-\frac{1}{2}} \sum_{\mu=1}^{6} \phi_\mu e^{\pi i \mu j/3}, \tag{114}$$

where ϕ_μ are the given AO of the $2pz$-type defined in (85).

Here we have used a conjugate complex description of the degenerate levels, but we note that the most general *real* representation of the coefficients C may be written in the form

$$C_\mu{}^i = \frac{1}{6^{\frac{1}{2}}} \cos \pi \mu j/3, \quad j = 0, 3 \tag{115}$$

$$C_\mu{}^{i\prime} = \frac{1}{\sqrt{3}} \cos(\alpha + \pi \mu j/3), \quad C_\mu{}^{i\prime\prime} = \frac{1}{\sqrt{3}} \sin(\alpha + \pi \mu j/3), \quad j = 1, 2$$

where α is an arbitrary real angle.

In order to prepare the treatment of the *perturbed* benzene molecule according to Sec. 3, we will now evaluate the fundamental quantities $d_{\mu\nu}{}^{jk}$, $\Omega_{\mu\nu}{}^j$, and $\pi_{\mu\nu, \kappa\lambda}{}^{jk}$ for the unperturbed molecule. According to (26) and (111), we obtain, in the conjugate complex description,

$$d_{\mu\nu}{}^{jk} = \frac{1}{6} \exp \pi i (k - j)(\mu + \nu)/6 \cdot \cos \pi (k + j)(\mu - \nu)/6, \tag{116}$$

which gives for the separate charge and bond orders

$$q_\mu{}^j = \tfrac{1}{6}, \quad p_\mu{}^j = \tfrac{1}{6} \cos \pi(\mu - \nu)j/3. \tag{117}$$

By using (48) and (111), we get further for $p = \nu - \mu$:

$$\Omega_{\mu\nu}{}^j = \Omega_{0, \nu-\mu}{}^j = \Omega_p{}^j = \tfrac{1}{6} \sum_{\alpha \neq (J)} \frac{\cos \pi p \alpha/3}{\epsilon^j - \epsilon^\alpha}, \tag{118}$$

where the denominators may be taken from (108) or (110). We note that, for each $j = 0, 1, 2$, and 3, there are only four independent elements $\Omega_p{}^j$. The mutabilities are then determined by the general formula (49):

$$\pi_{\mu\nu, \kappa\lambda}{}^{jk} = \frac{1}{2}(d_{\mu\kappa}{}^{jk}\Omega_{\nu-\lambda}{}^j + d_{\mu\lambda}{}^{jk}\Omega_{\nu-\kappa}{}^j$$

$$+ d_{\nu\kappa}{}^{jk}\Omega_{\mu-\lambda}{}^j + d_{\nu\lambda}{}^{jk}\Omega_{\mu-\kappa}{}^j); \tag{119}$$

which for $j = k$ gives

$$\pi_{\mu\nu, \kappa\lambda}{}^{jj} = \frac{1}{12}\{\Omega_{\mu-\kappa}{}^j \cos\pi(\nu - \lambda)/3$$

$$+ \Omega_{\mu-\lambda}{}^j \cos\pi(\nu - \kappa)/3 + \Omega_{\nu-\kappa}{}^j \cos\pi(\mu - \lambda)/3$$

$$+ \Omega_{\nu-\lambda}{}^j \cos\pi(\mu - \kappa)/3\}. \tag{120}$$

All the quantities fundamental for a second-order perturbation theory are then evaluated, and the results in Sec. 3 can be directly applied to computing the properties of the perturbed ring. All these results are of a general nature and may be taken over also in a more elaborate MO-theory of the perturbed benzene molecule.

6. The "Nearest Neighbor" Approximation in the Naïve Molecular Orbital Theory

In addition to the general theory given in the previous section, we will now consider in greater detail the "nearest neighbor" approximation in the naïve MO-theory of the perturbed benzene ring. This type of approximation, which is sometimes also called the "tight-binding" approximation, seems to have been first introduced by Bloch[31] in the band theory of metals. It is based on the assumption that, in the matrices S and H with respect to the given AO, only the elements associated with the same or adjacent atoms are of importance, whereas elements associated with a pair of higher neighborhood may be neglected. This approximation is characterized by a high simplicity, but it is certainly not very accurate.

The fundamental matrices (106) are in this approximation of the simple form

$$H = (\alpha, \beta, 0, 0, 0, \beta)_{\text{cyclic}}$$
$$S = (0, S, 0, 0, 0, S)_{\text{cyclic}}. \tag{121}$$

For S we will use the values $S = 0$ (overlap neglected) and $S = 0.25$, and further we will use the quantity $\gamma = \beta - \alpha S$. We note that it is easy to evaluate any given function of the matrix S according to formula (104), and, as examples, we give the matrices

$$(1+S)^{-1} = (1.1555; -0.3111; 0.0888; -0.0444; 0.0888; -0.3111)_{\text{cyclic}},$$

$$(1+S)^{-\frac{1}{2}} = (1.0548; -0.1430; 0.0303; -0.0129; 0.0303; -0.1430)_{\text{cyclic}}, \tag{122}$$

for $S = 0.25$, which may be useful in treating a molecule having about the same overlapping scheme as benzene.

We observe that the "nearest neighbor" approximation is explicitly based on an assumption concerning the extension of the given AO, which means that it cannot be generalized with the same degree of accuracy to matrices with respect to the ON-AO, which usually have much larger extensions. The matrix H', evaluated

TABLE II.

j	$S=0$	$S=0.25$
0	$\alpha+2\beta$	$\alpha+1.3333\gamma$
± 1	$\alpha+\beta$	$\alpha+0.8\gamma$
± 2	$\alpha-\beta$	$\alpha-1.3333\gamma$
3	$\alpha-2\beta$	$\alpha-4\gamma$

(124)

from (107), (121), and (122), has also the form

$$\mathbf{H'} = (\alpha - 0.6222\gamma; 1.2444\gamma; -0.3555\gamma;$$
$$0.1777\gamma; -0.3555\gamma; 1.2444\gamma)_{\text{cyclic}}, \quad (123)$$

showing also interaction between ON-AO of higher neighborhood. The matrix (123) was first given in another way by Chirgwin and Coulson.[12]

According to (108) and (110), we obtain the values for the orbital energies ϵ^j of the unperturbed molecule, which are listed in Table II. Hence, the symmetry around the point $\epsilon = \alpha$ is disturbed by the inclusion of the overlap. The matrix $\mathbf{d}$ is given by (116), and, by using (118) and (124), we obtain the values of the quantities $\Omega_p{}^j$ which are presented in Table III. The mutabilities $\pi_{\mu\nu,\kappa\lambda}{}^{jj}$ can then be evaluated by means of (120), and the results for $S=0$ are given in Table IV. As we will see later, the alternating signs in the series of total atom-atom mutabilities for the ground state will render an explanation of the chemical law of "alternating polarity" for benzene. The total atom-bond mutabilities are zero, in agreement with a general theorem given by Coulson and Longuet-Higgins.[5]

In Table V, we have presented a comparison between the values of the separate mutabilities $\pi_{\mu\nu,\kappa\lambda}{}^{jj}$ for $S=0$ and $S=0.25$. The series of total atom-atom mutabilities was first given for $S=0.25$ by Chirgwin and Coulson,[12] who remarked that, except for the change in unit from $1/\beta$ to $1/\gamma$, these total quantities are only slightly affected by the inclusion of the overlap. However, even if this is true for the total mutabilities, the table shows that the *separate* mutabilities are rather strongly changed when going over from $S=0$ to $S=0.25$. This

TABLE III(a). The quantities $\Omega_p{}^j$ in units of $1/72\beta$ for $S=0$.

$\diagdown$	0	1	2	3
0	35	5	−13	−19
1	4	−22	−14	−4
2	−4	−22	14	−4
3	−35	5	13	−19

TABLE III(b). The quantities $\Omega_p{}^j$ in units of $1/576\gamma$ for $S=0.25$.

$\diagdown$	0	1	2	3
0	450	126	−198	−306
1	−70	−245	−205	−110
2	−90	−117	45	18
3	−130	−2	38	−50

means that if, for instance, the *frontier* electrons turn out to have particular importance, then the overlap must be included from the very beginning, particularly when treating heteromolecules. Finally, we note that there are a series of simple identities and check relations for the mutabilities, which may be derived by considering such perturbations as leave the orbital energies unchanged.

Charge and Bond Orders of the Perturbed Benzene Ring—the Directing Power of a Perturbation

For the sake of simplicity, let us first consider the case of overlap neglected, $S=0$. Let further the perturbations $V_{\mu\nu}$, defined by (31), be given as fractions of the quantity β:

$$V_{\mu\mu} = \delta_\mu\beta, \quad V_{\mu\nu} = \vartheta_{\mu\nu}\beta \quad (\mu \neq \nu). \quad (125)$$

According to the general formula (72) and Table IV, we obtain for the *total charge orders* q_μ associated with the ground state,

$$q_1 = 1 + (43\delta_1 - 17\delta_2 + \delta_3 - 11\delta_4 + \delta_5 - 17\delta_6)/108,$$
$$q_2 = 1 + (43\delta_2 - 17\delta_3 + \delta_4 - 11\delta_5 + \delta_6 - 17\delta_1)/108,$$
$$\cdots \text{ and cyclic. } \quad (126)$$

A special case of these formulas was first given by Wheland and Pauling,[3] and the coefficients in general may be found in Coulson and Longuet-Higgins.[5] Since all atom-bond mutabilities are zero, all the charge orders are independent of the perturbations $\vartheta_{\mu\nu}$ of the bond affinities.

As was mentioned previously in Sec. 2, the total charge orders were first utilized by Wheland and Pauling for investigating the "directing power" of a perturbation, and here we will add a few remarks concerning this problem for the perturbed benzene ring. Since a cationoid reagent is always electron-seeking, it seems natural to assume that a substitution of such a reagent will take place preferentially at that carbon atom of the ring, which has the largest negative charge.[33] The atom-atom mutabilities of Table IV show now that, for $\delta_\mu > 0$, there will be a large increase of the electron density at the place μ of the perturbation and that the perturbation will cause also a slight increase of the density at the *meta*-position and comparatively large decreases at the *ortho*- and *para*-positions (*meta*-directing power). For $\delta_\mu < 0$, the conditions will be changed (*ortho-para*-directing power).

The alternating signs in the row for the total atom-atom mutabilities seem therefore to give an explanation of the chemical law of *alternating polarity* for the perturbed ring. The same law holds probably in general for all conjugated systems, and here it may therefore be of some interest to test explicitly for benzene the validity of the idea mentioned previously by Lennard-Jones[4] and by Fukui, Yonezawa, and Shingu[17] that the

[33] See reference 26, p. 149.

TABLE IV. Separate mutabilities $\pi_{\mu\nu,\kappa\lambda}^{jj}$ in units of $1/216\beta$ for $S=0$.

Indexes j	Atom-atom				Atom-bond			Bond-bond			
	11.11	11.22	11.33	11.44	11.12	11.23	11.34	12.12	12.23	12.34	12.45
0	35	5	−13	−19	20	−4	−16	20	8	−10	−16
±1	4	−11	7	4	−10	2	8	−3.5	−9.5	8.5	5.5
±2	−4	11	−7	−4	−10	2	8	3.5	9.5	−8.5	−5.5
3	−35	−5	13	19	20	−4	−16	−20	−8	10	16
total[a]	86	−34	2	−22	0	0	0	26	−22	14	−10

[a] Total = twice the sum of the contributions from the orbitals 0 and ±1, associated with the ground state.

alternating character should depend mainly on the properties of the highest occupied orbital in the ground state. In Table IV, we can find the contributions to the total atom-atom mutabilities from the different occupied orbitals, and the phenomenon of the alternating signs is here due to the combined effect of the lowest orbital and the next two higher orbitals.[33a] The particular importance of the frontier electrons may be true for more complicated conjugated compounds, but Table IV shows that it is not valid for the simple case of benzene.

The simple theory of directing power by Wheland and Pauling was slightly complicated by the observation that most *ortho-para*-directing perturbations also activate the ring in comparison to benzene, and that most *meta*-directing perturbations deactivate the ring. In order to obtain even this effect, Wheland and Pauling[3] assumed that each perturbation A, in addition to the perturbation δ_A in its own position, causes also smaller perturbations $\delta_A' = \kappa\delta_A$ in the positions of the adjacent atoms. According to (126), this activation condition is fulfilled and the nature of the directing power is preserved, if κ satisfies the inequality, $1/28 < \kappa < 1/4$. Wheland and Pauling proposed the reasonable value $\kappa = 1/10$, but, following Nordheim and Sponer,[34] we will here use the value $\kappa = 1/8$. Still other values are in use.[35]

We can now treat the question of the different reactivities of the carbon atoms in a perturbed benzene ring by formula (126), where for $\mathcal{E}_\mu$ ($\mu = 1, 2, \cdots, 6$) we take the values obtained by summing the contributions from the perturbations $A, B, \cdots$ introduced in the ring.

By using the general formula (72) and Table IV, we obtain further, for the *total bond orders* p_μ, associated with the ground state,

$$p_{12} = \tfrac{2}{3} + (13\vartheta_{12} - 11\vartheta_{23} + 7\vartheta_{34} - 5\vartheta_{45} + 7\vartheta_{56} - 11\vartheta_{61})/108,$$

$$p_{23} = \tfrac{2}{3} + (13\vartheta_{23} - 11\vartheta_{34} + 7\vartheta_{45} - 5\vartheta_{56} + 7\vartheta_{61} - 11\vartheta_{12})/108,$$

(127)

$\cdots$ and cyclic.

After computing these bond orders, the *bond lengths* may be found according to the semi-empirical scheme described by Coulson and Longuet-Higgins. We note that even (127) gives rise to properties of alternating character. Since all total bond-atom mutabilities are zero, the total bond orders are entirely independent of the perturbations δ_μ in the charge affinities. This implies that, since the quantities ϑ_μ usually may be considered as rather small, the bond orders and hence the

TABLE V. Comparison between separate mutabilities $\pi_{\mu\nu,\kappa\lambda}^{jj}$ in units of $1/\beta$ for $S=0$, and in units of $1/\gamma$ for $S=0.25$.

j	S	Atom-atom				Atom-bond			Bond-bond			
		11.11	11.22	11.33	11.44	11.12	11.23	11.34	12.12	12.23	12.34	12.45
0	0	0.16204	0.02315	−0.06019	−0.08796	0.09259	−0.01852	−0.07407	0.09259	0.03704	−0.04630	−0.07407
	0.25	0.26042	0.07292	−0.11458	−0.17708	0.16667	−0.02083	−0.14583	0.16667	0.07292	−0.08333	−0.14583
±1	0	0.01852	−0.05093	0.03241	0.01852	−0.04630	0.00926	0.03704	−0.01620	−0.04398	0.03935	0.02546
	0.25	−0.04051	−0.07089	0.05932	0.06366	−0.08102	0.00579	0.07523	−0.05570	−0.06004	0.05715	0.06149
±2	0	−0.01852	0.05093	−0.03241	−0.01852	−0.04630	0.00926	0.03704	0.01620	0.04398	−0.03935	−0.02546
	0.25	−0.05208	0.03385	−0.01302	0.01042	−0.02083	0.01042	0.01042	−0.00911	0.02995	−0.02474	−0.00130
3	0	−0.16204	−0.02315	0.06019	0.08796	0.09259	−0.01852	−0.07407	−0.09259	−0.03704	0.04630	0.07407
	0.25	−0.07523	0.00116	0.02199	0.02894	0.03704	−0.01157	−0.02546	−0.03704	−0.01273	0.01852	0.02546
total[a]	0	0.39814	−0.15740	0.00926	−0.10186	0	0	0	0.12038	−0.10186	0.06482	−0.04630
	0.25	0.35880	−0.13774	0.00810	−0.09954	0.00926	−0.01852	0.00926	0.11054	−0.09432	0.06192	−0.04572

[a] The total quantities are referred to the ground state.

[33a] *Note added in proof:* Compare also H. H. Greenwood, J. Chem. Phys. 20, 1653L (1952).
[34] G. P. Nordheim and H. Sponer, J. Chem. Phys. 20, 285 (1952).
[35] H. H. Jaffé, J. Chem. Phys. 20, 279, 778 (1952) has used the large value $\kappa = 1/3$ together with the assumption that even higher neighbors are affected according to a geometrical progression in κ.

TABLE VI. Dipole moments of some heterocyclics containing nitrogen in Debye units ($= 10^{-18}$ esu). $\delta_N = 0.6$.

Compound	Calculated π-moment	Calculated σ-moment	Dipole moment calculated	Dipole moment observed[a]
Pyridine	1.51	0.85	2.36	2.22
Pyridazine	2.60	1.48	4.08	3.94
Pyrimidine	1.51	0.85	2.36	2.42
Pyrazine	0	0	0	0

[a] The observed data are taken from Wesson's compilation: L. G. Wesson. *Tables of Electric Dipole Moments* (Massachusetts Institute of Technology, 1948).

bond lengths are only slightly affected by perturbations of the ring. This is in agreement with experience.

We have here investigated only the case $S=0$, but the corresponding formulas for $S=0.25$ are easily written up by using (72) and Table V. We note that, in the latter case, the perturbations $V_{\mu\nu}$, defined by (31), must be given as fractions of the quantity γ:

$$V_{\mu\mu} = \delta_\mu \gamma, \quad V_{\mu\nu} = \vartheta_{\mu\nu}\gamma \quad (\mu \neq \nu). \quad (128)$$

When overlap is included, there is a slight complication of the theory depending on the fact that the charge orders q_μ are strictly speaking associated with the ON-AO φ_μ, and these orbitals are only semilocalized on the atoms μ.[36] However, since the whole naïve MO-theory is in all events very crude, we believe that the quantities q_μ and $p_{\mu\nu}$ may be used and "interpreted" in the semi-empirical theory in the same way as before.

In this connection, we observe that, since the advantage of the naïve theory is just its simplicity, it is in general impossible to improve the theory within its own frame. An essential improvement can first be obtained by studying a much more elaborate theory, based on antisymmetrized molecular wave functions, but, also in this case, many of the quantities treated here will still be useful.

Calculation of Dipole Moments of the Perturbed Benzene Ring[37]

We shall now investigate the contributions from the π-electrons to the dipole moment of the perturbed benzene ring. Since the total charge of the π-electrons is different from zero, it is convenient to use the symmetry center of the ring as fixed reference point and origin of the coordinate system.

Let us first consider the simple case $S=0$. In the naïve MO-theory, the total π-electron charges at the various atoms are given by the quantities eq_μ determined by (126). Since these relations are linear in the first-order approximation, it is sufficient to consider only one of the perturbations δ_μ. According to (127), the bond lengths are only slightly affected by the

perturbations introduced in the ring, and we will therefore use a constant bond length a equal to the benzene value ($a = 1.40 \times 10^{-8}$ cm) and a hexagonal form of the ring. From (126), it is then easily shown that each perturbation gives rise to a vector contribution to the π-moment of the magnitude $ea\delta_\mu/3$ esu with the direction from the center to the atom μ. Using the value $e = 4.80 \times 10^{-10}$ esu, this gives a vector contribution of

$$2.24\,\delta_\mu \text{ Debye units} \quad (129)$$

for each perturbation. However, each heteroatom or group A introduced in a specific position in the ring causes, in addition to δ_A, also smaller perturbations $\delta_{A}' = \delta_A/8$ in the adjacent positions, and the resulting vector contribution from A is therefore

$$2.52\,\delta_A \text{ Debye units.} \quad (130)$$

Thus we have found theoretically that the ordinary *vector addition rule* for calculating dipole moments holds even for the contributions from the *mobile* π-electrons of the perturbed benzene ring. In order to find the total dipole moment of the molecule, we have then only to add the contribution from the σ-electrons with respect to the center, determined by the vector rule from the bond moments.

As examples, we will consider perturbed benzene rings containing nitrogen or methyl-groups. If in pyridine, C_5H_5N, the value $\delta_N = 2$, recommended by Wheland and Pauling[3] is used, formula (130) gives a π-moment of 5.04 D; a more exact solution of the secular equation gives 4.48 D. Both these values are much too high to be in agreement with the observed data, and thus δ_N and then the whole δ-scale must be essentially reduced in value in order to correspond to the correct dipole moments. We have found a value of $\delta_N = 0.6$ more reasonable, and in Table VI we have summarized our results for pyridine and the diazines in comparison to the experimental values. Our δ_N-value is supported by a recent paper by Orgel et al.,[38] where it is shown by solving the secular equation that a value of $\delta_N = 1.0$ gives π-moments which are too high by a factor 1.6.

We will further investigate some benzene derivatives containing a methyl group. Neglecting hyperconjugation, the influence of the methyl group is treated as only causing a perturbation δ_{CH_3} at the carbon atom of the ring, where it is attached. From chemical observations, it is a well-known fact that nitrogen in pyridine is meta-directing, whereas the methyl group in toluene is ortho-paradirecting; the former corresponds to a positive value of δ_N and the latter to a negative value of δ_{CH_3}. By using the value $\delta_{CH_3} = -0.10$, we have obtained the results for toluene, the xylenes, and the picolines listed in Table VII.

In this investigation, two adjustable parameters give values of the dipole moments of eleven molecules in good

[36] See also R. McWeeny, J. Chem. Phys. **19**, 1614 L (1951) with errata in J. Chem. Phys. **20**, 920 L (1952).

[37] For a preliminary report of the results in this section, see P. O. Löwdin, J. Chem. Phys. **19**, 1323 L (1951).

[38] Orgel, Cottrell, Dick, and Sutton, Trans. Faraday Soc. **47**, 113 (1951).

agreement with experience. The naïve MO-theory gives us here a device for correlating the observed chemical properties of directing power with the values of the dipole moments. We note particularly the increase of the dipole moment from pyridine to γ-picoline, which is associated with the difference in sign between δ_N and δ_{CH_3}, i.e., with the difference in directing power.

Here we have discussed only the naïve MO-theory in the simple case when overlap is neglected ($S=0$), but now we will derive also a more exact expression for the dipole moment of the π-electrons. For this purpose we will consider the *bonding-overlapping* matrix $\mathbf{R}$ introduced in reference 20, p. 1572, by the formula

$$\mathbf{R}=(1+S)^{-\frac{1}{2}}\mathbf{d}^{tot}(1+S)^{-\frac{1}{2}}, \tag{131}$$

or

$$R_{\mu\nu}=\sum_{\alpha\beta}(1+S)_{\mu\alpha}^{-\frac{1}{2}}d_{\alpha\beta}^{tot}(1+S)_{\beta\nu}^{-\frac{1}{2}}. \tag{132}$$

We describe the system of π-electrons in the ground state by an antisymmetrized molecular wave function, Ψ, which is approximated by a determinant of molecular spin-orbitals (MSO) formed by taking the product of the MO ψ^i and the ordinary spin functions. The π-moment is then

$$\mathbf{D}_\pi=e\int\Psi^*\mathbf{x}\Psi(d\tau). \tag{133}$$

This expression can be simplified in the following way by using (131):

$$\mathbf{D}_\pi=2e\sum_j^{occ}\int\psi^{i*}\mathbf{x}\psi^i d\tau$$

$$=2e\sum_j^{occ}\sum_{\mu\nu}C^{\dagger i}{}_\mu\int\varphi_\mu\mathbf{x}\varphi_\nu d\tau\cdot C_\nu{}^i$$

$$=2e\sum_j^{occ}\sum_{\mu\nu}d_{\nu\mu}{}^{ii}\int\varphi_\mu\mathbf{x}\varphi_\nu d\tau$$

$$=e\sum_{\mu\nu}d_{\nu\mu}{}^{tot}\int\varphi_\mu\mathbf{x}\varphi_\nu d\tau$$

$$=e\sum_{\mu\nu,\alpha\beta}d_{\nu\mu}{}^{tot}(1+S)_{\mu\alpha}^{-\frac{1}{2}}\int\phi_\alpha\mathbf{x}\phi_\beta d\tau(1+S)_{\beta\nu}^{-\frac{1}{2}}$$

$$=e\sum_{\alpha\beta}\{\sum_{\mu\nu}(1+S)_{\beta\nu}^{-\frac{1}{2}}d_{\nu\mu}{}^{tot}(1+S)_{\mu\alpha}^{-\frac{1}{2}}\}\int\phi_\alpha\mathbf{x}\phi_\beta d\tau$$

$$=e\sum_{\alpha\beta}R_{\beta\alpha}\int\phi_\alpha\mathbf{x}\phi_\beta d\tau, \tag{134}$$

which gives the formula

$$\mathbf{D}_\pi=e\sum_{\mu\nu}R_{\nu\mu}\int\phi_\mu\mathbf{x}\phi_\nu d\tau. \tag{135}$$

TABLE VII. Dipole moments of some benzene derivatives containing nitrogen and methyl, in Debye units. $\delta_N=0.6$ and $\delta_{CH_3}=-0.1$.

Compound	Dipole moments		Compound	Dipole moments	
	calculated	observed[a]		calculated	observed[a]
Toluene	0.25	0.37			
o-xylene	0.44	0.52	α-picoline	2.49	1.72
m-xylene	0.25	0.37	β-picoline	2.25	2.30
p-xylene	0	0	γ-picoline	2.61	2.57

[a] See reference a, Table VI.

In order to compute the π-moment, we have therefore to calculate the total charge and bond orders, q_μ and $p_{\mu\nu}$, which form the elements of the matrix $d_{\mu\nu}{}^{tot}$, and after inclusion of the overlap matrix S according to (131), we can then find the π-moments if the integrals $\int\phi_\mu\mathbf{x}\phi_\nu d\tau$ are known. We note that the quantities q_μ and $p_{\mu\nu}$ still play a fundamental role, but that more information about the molecule is needed here than in the naïve theory.

Calculation of Orbital Energies for the Perturbed Benzene Ring

The orbital energies are of particular importance for investigating various properties of the molecule as a whole. We observe that the orbital energies cannot be directly used for evaluating excitation energies, since, for this purpose, they have to be completed with information about the separate "repulsion integrals," but that they give the *ionization energies* of the perturbed molecule according to Koopmans' theorem[39] with a high degree of accuracy.[40]

The orbital energies ϵ^i for the perturbed benzene ring can easily be obtained to the second order by means of the perturbation scheme developed in Sec. 3. According to Eqs. (52) and (80), we obtain for the nondegenerate and the doubly degenerate levels, respectively:

$$\epsilon^i=U^{ii}, \qquad j=0, 3,$$
$$\epsilon^i=U^{ii}\pm|U^{ii'}|, \quad j=\pm1, \pm2. \tag{136}$$

where the elements U^{ik} are given by (46). As an example we will tabulate the orbital energies for the sim-

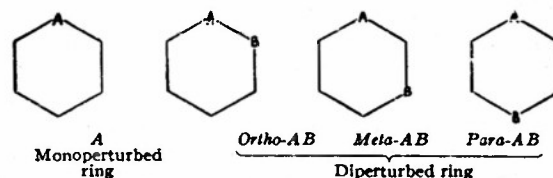| A Monoperturbed ring | Ortho-AB | Meta-AB | Para-AB |
| | Diperturbed ring | | |

FIG. 3. Types of perturbations introduced in the ring. In addition to the perturbations δ_A and δ_B in the positions of A and B, respectively, there are also smaller perturbations $\delta_A'=\delta_A/8$ and $\delta_B'=\delta_B/8$ in the adjacent positions.

[39] T. Koopmans. Physica 1, 104 (1934). See also C. C. J. Roothaan, Revs. Modern Phys. 23, 69 (1951).
[40] See the discussion given by Mulliken in R. S. Mulliken, J. chim. phys. 46, 497 (1949).

ple cases of a ring containing one or two perturbations, A and B, according to Fig. 3.

For the sake of simplicity, only the case of perturbed charge affinities for $S=0$ will be treated explicitly, i.e.,

$$V_{\mu\mu}=\delta_\mu\beta, \quad V_{\mu\nu}=0 \quad (\mu\neq\nu). \qquad (137)$$

The more general problem can be solved in the same way without any difficulties. The actual matrix elements U^{jj} and $U^{jj'}$ $(j'=-j)$ have now the form

$$U^{jj}=\epsilon^{j(0)}+\frac{\beta}{6}\sum_\mu \delta_\mu+\frac{\beta^2}{2}\sum_{\mu\kappa}\delta_\mu\delta_\kappa\pi_{\mu\mu,\,\kappa\kappa}{}^{jj},$$

$$\qquad (138)$$

$$U^{jj'}=\frac{\beta}{6}\sum_\mu \delta_\mu e^{-2\pi i\mu j/3}+\frac{\beta^2}{6}\sum_{\mu\kappa}\delta_\mu\delta_\kappa\Omega_{\mu-\kappa}{}^j e^{-\pi i(\mu+\kappa)j/3},$$

and, for the real and imaginary parts of $U^{jj'}$, we get specifically

$$Re\{U^{jj'}\}=\frac{\beta}{6}\sum_\mu \delta_\mu \cos2\pi\mu j/3$$
$$\qquad +\frac{\beta^2}{6}\sum_{\mu\kappa}\delta_\mu\delta_\kappa\Omega_{\mu-\kappa}{}^j \cos\pi(\mu+\kappa)j/3,$$

$$\qquad (139)$$

$$I\{U^{jj'}\}=-\frac{\beta}{6}\sum_\mu \delta_\mu \sin2\pi\mu j/3$$
$$\qquad -\frac{\beta^2}{6}\sum_{\mu\kappa}\delta_\mu\delta_\kappa\Omega_{\mu-\kappa}{}^j \sin\pi(\mu+\kappa)j/3,$$

TABLE VIII. Orbital energies for a monoperturbed ring for $S=0$ and $\delta_{A}'=\delta_A/8$: $\epsilon^j=\alpha+\beta(\tau^j+c_A{}^j\delta_A+c_{AA}{}^j\delta_A{}^2)$.

j	τ^j	$c_A{}^j$	$c_{AA}{}^j$
0	2	0.20833	0.08840
1'	1	0.35417	−0.00731
1''	1	0.06250	0.00195
2'	−1	0.35417	0.00731
2''	−1	0.06250	−0.00195
3	−2	0.20833	−0.08840

TABLE IX. Comparison between values of the orbital energies[a] for a monoperturbed ring, obtained by means of perturbation theory (PT) or by solving the secular equation (SE): $\delta_A=0.5$, 1, 1.5, and 2.

j	Method	$\delta_A=0.5$	$\delta_A=1$	$\delta_A=1.5$	$\delta_A=2$
0	PT	2.126	2.297	2.511	2.770
	SE	2.130	2.322	2.584	2.907
1'	PT	1.175	1.347	1.515	1.679
	SE	1.172	1.319	1.431	1.510
1''	PT	1.031	1.064	1.098	1.133
	SE	1.031	1.064	1.098	1.133
2'	PT	−0.821	−0.639	−0.452	−0.262
	SE	−0.824	−0.659	−0.512	−0.383
2''	PT	−0.969	−0.939	−0.911	−0.883
	SE	−0.969	−0.939	−0.911	−0.883
3	PT	−1.918	−1.880	−1.886	−1.937
	SE	−1.915	−1.857	−1.816	−1.735

[a] $(\epsilon-\alpha)/\beta$.

and thereafter the angle 2φ in (84), which determines the coefficients in the perturbed MO.

The results for a monoperturbed benzene ring are given in Table VIII, and, in Table IX, we have given a comparison between the energies obtained according to second-order perturbation theory (PT) and the energies obtained by solving the secular equation (SE). In the last table, only the quantities $(\epsilon-\alpha)/\beta$ are listed. We note that the perturbation theory shows excellent agreement with the SE-values in the region $\delta_A=0.5$, and that the accuracy is sufficient for most purposes in the naïve theory also around the point $\delta_A=1$.

In Table X we have finally listed the orbital energies for a diperturbed benzene ring with $S=0$ and $\delta_A'=\delta_A/8$, $\delta_B'=\delta_B/8$. The energies are here expressed in the form:

$$\epsilon^j=\alpha+\beta x^j,$$

$$x^j=\tau^j+c_A{}^j\delta_A+c_B{}^j\delta_B+\bar{c}^j\delta$$
$$\qquad +c_{AA}{}^j\delta_A{}^2+c_{AB}{}^j\delta_A\delta_B+c_{BB}{}^j\delta_B{}^2 \qquad (140)$$
$$\qquad +(\bar{c}_{AA}{}^j\delta_A{}^3+\bar{c}_{AB}{}^j\delta_A{}^2\delta_B+\bar{c}_{BA}{}^j\delta_A\delta_B{}^2+\bar{c}_{BB}{}^j\delta_B{}^3)/\delta,$$

$$\delta=(\delta_A{}^2-\delta_A\delta_B+\delta_B{}^2)^{\frac12}.$$

The results given in Tables VIII and X will be utilized in subsequent papers.

A discussion of the *symmetry properties* of the mono- and diperturbed benzene ring has recently been given by Nordheim and Sponer,[34] who have also investigated the molecular orbitals and the orbital energies of some compounds of these types by solving the secular equations.

7. Concluding Remarks

The general second-order perturbation theory for perturbed conjugated systems, developed in the first part of this paper, seems to have a sufficient accuracy for most applications in the semi-empirical theory. If the basic MO-properties of, e.g., a parent hydrocarbon are known, it is possible to derive the corresponding properties of a heterocompound, obtained by replacing one or more carbon atoms by heteroatoms or groups, in a rather simple way without the laborious solution of higher order secular equations with different elements.

For small perturbations $(\delta<1)$, the same perturbation scheme may be used also in a more elaborate MO-theory, and, for larger perturbations, one has the possibility of improving the accuracy by the inclusion of terms of the third and higher orders.

In the second part of the paper, the theory has been applied to the perturbed benzene ring having six π-orbitals, and a number of useful "benzene constants" have been tabulated. We note that, by splitting the secular equation in a way recently described by the author,[21] it is possible to transform problems concerning substituted benzenes having seven, eight, or more π-orbitals, into a form where they are closely related to the

TABLE X. Orbital energies for a diperturbed benzene ring with $S=0$, $\delta_A' = \delta_A/8$, and $\delta_B' = \delta_B/8$, according to formula (140).

Compound	j	τ	$c_A^j = c_B^j$	$\tilde{c}^j$	$c_{AA}^j = c_{BB}^j$	c_{AB}^j	$\tilde{c}_{AA}^j = \tilde{c}_{BB}^j$	$\tilde{c}_{AB}^j = \tilde{c}_{BA}^j$
Ortho-AB	0	2	0.20833	...	0.08840	0.04832	...	...
	1'	1	0.20833	0.14583	−0.00268	−0.04029	−0.00463	−0.05165
	1''	1	0.20833	−0.14583	−0.00268	−0.04029	0.00463	0.05165
	2'	−1	0.20833	0.14583	0.00268	0.04029	0.00463	0.05165
	2''	−1	0.20833	−0.14583	0.00268	0.04029	−0.00463	−0.05165
	3	−2	0.20833	...	−0.08840	−0.04832	...	...
Meta-AB	0	2	0.20833	...	0.08840	−0.07668	...	...
	1'	1	0.20833	0.14583	−0.00268	0.02611	−0.00463	0.04210
	1''	1	0.20833	−0.14583	−0.00268	0.02611	0.00463	−0.04210
	2'	−1	0.20833	0.14583	0.00268	−0.02611	0.00463	−0.04210
	2''	−1	0.20833	−0.14583	0.00268	−0.02611	−0.00463	0.04210
	3	−2	0.20833	...	−0.08840	0.07668	...	...
Para-AB	0	2	0.20833	...	0.08840	−0.12008	...	...
	1'	1	0.35417	...	−0.00731	0.07133	...	...
	1''	1	0.06250	...	0.00195	−0.00390	...	...
	2'	−1	0.35417	...	0.00731	−0.07133	...	...
	2''	−1	0.06250	...	−0.00195	0.00390	...	...
	3	−2	0.20833	...	−0.08840	−0.12008	...	...

benzene problem treated here, and where the same "benzene constants" may again be useful.

Wavelength Shifts in the near Ultraviolet Spectra of Fluorinated Benzenes

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Results on wavelength shifts of the 0,0 bands in the near ultraviolet absorption spectra of a number of fluorinated benzenes are presented, and a brief discussion in terms of the inductive effect and the migration effect is added.

IT has been observed that the electronic transition which occurs in benzene at 2600A shifts toward longer wavelengths upon substitution. This shift has been the subject of many studies and was discussed, usually together with the intensity of the absorption spectra, in its dependence upon the resonance interaction between ring and substituent (migration effect, mesomeric effect) and upon the polarity of the ring-substituent bond (inductive effect).[1] In general, the results on intensities[1b,1c,2] have been more satisfactory than those on wavelength shifts.

We have made in our laboratory some interesting observations on wavelength shifts in the spectra of fluorinated benzenes. The most unusual result was obtained for 1,3,5-trifluorobenzene.[3] Unlike the cases of other substitutions studied spectroscopically, in which the spectrum of the trisubstituted derivative shifts further to the red as compared to that of the mono-derivative (see for example 1,3,5-trichlorobenzene[4] in Table I), the spectrum of 1,3,5-trifluorobenzene shifts toward the violet as compared to the fluorobenzene spectrum. In fact, it even lies at shorter wavelengths than the benzene spectrum. Although the analysis has been carried through only partially so far, it can be said that the calculated position of the 0,0 band is probably at 38 527 cm^{-1}. This means that introduction of two more fluorine atoms in the 3 and 5 positions over-compensates the small red shift for fluorobenzene, causing a total shift of 708 cm^{-1} to the violet with respect to the 0,0 band in fluorobenzene. We believe this to be the first example of this type. The spectrum has the intensity and the appearance characteristic of a transition forbidden by symmetry, as is to be expected for the first absorption of a symmetrical trisubstituted benzene molecule and as has been found to be the case for 1,3,5-trimethylbenzene and 1,3,5-trichlorobenzene.

Subsequent investigation of the near ultraviolet spectrum of 1,3,5-tris-trifluoromethylbenzene[5] gave as probable position of the nonobservable 0,0 band 38 100 cm^{-1}, that is, it is shifted towards shorter wavelengths not only with respect to benzotrifluoride, but also with respect to benzene (Table I).

Another interesting example offers the series fluorobenzene, p-difluorobenzene,[6] 1,2,4-trifluorobenzene,[7] where the 0,0 band of the p-diderivative moves toward the red and that of the 1,2,4-triderivative shifts a little back toward the position of the 0,0 band of the mono-derivative. The corresponding transitions in chlorinated benzenes, added for comparison in Table I, show a continued red shift from the mono- to the trisubstituted compounds.

The observations on the shifts suggest that they are the result of the combined action of two effects. In the first effect, the fluorine because of its large electron affinity attracts σ electrons from the ring (inductive effect), in the second effect, charge from the non-bonding $2p\pi$ electrons of the substituent can migrate into the ring (migration effect).† Because of the very high ionization potential of the fluorine atom, the second effect is very small. The effects are opposite in sign. They will not only influence the charge of the fluorinated carbons, but also the charge of the whole frame in which the mobile π electrons travel. If the migration effect predominates, the negative charge added to the ring will decrease the potential field in which the π electrons move; if, on the other hand, the effect resulting from the electron affinity is greater, the ring potential increases.‡ Thus, in the first case the absorption spectrum will show a red shift and in the second case a blue shift. In multiple substitutions, the arrangements producing the smallest migration effect will give the largest blue shift. In the trisubstituted fluorobenzenes this is,

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[1] (a) K. F. Herzfeld, Chem. Revs. **41**, 233 (1947); (b) A. L. Sklar, J. Chem. Phys. **7**, 984 (1939); *ibid.* **10**, 135 (1942); (c) Th. Förster, Z. Naturforsch. **2a**, 149 (1947); (d) F. A. Matsen, J. Am. Chem. Soc. **72**, 5243 (1950); (e) W. W. Robertson and F. A. Matsen, J. Am. Chem. Soc. **72**, 5252 (1950).

[2] John R. Platt, J. Chem. Phys. **19**, 263 (1951).

[3] M. L. N. Sastri, Ph.D. dissertation, Duke University, 1951.

[4] H. Sponer and M. D. Hall, V. Henri Memorial Vol. Contributions à l'Etude de la Structure Moléculaire, Desoer 1947–1948, p. 211.

[5] C. D. Cooper and F. W. Noegel, J. Chem. Phys. **20**, 1903 (1952).

[6] C. D. Cooper, Phys. Rev. **91**, 241 (A) (1953). The solution spectrum was taken by A. Wenzel and H. P. Stephenson at our laboratory.

[7] Vapor and solution spectra were first obtained by H. P. Stephenson and are now being studied in more detail by K. N. Rao in our laboratory.

† The π electrons can also be attracted in the inductive effect, but the migrational effect is considered more important for them.

‡ The views presented here lie somewhat along the lines recently put forward by C. A. Coulson [Proc. Phys. Soc. (London) **65**, 933 (1952)] in his treatment of alkyl shifts in absorption spectra of azulenes. See also Pullman, Mayot, and Berthier, J. Chem. Phys. **18**, 257 (1950) and H. C. Longuet-Higgins and R. G. Snowden, Jr., J. Chem. Soc. **1952**, 1404.

for example, the case for the 1,3,5-arrangement, but in the 1,2,4-compound the migrational effect outweighs the inductive effect. The chlorobenzenes will always give a red shift, as not only is the electron affinity of the Cl atom smaller than that of the F atom, but it also has a much smaller ionization potential, which will increase the migrational effect.

Förster has given a semi-empirical formula for the wavelength shift in substituted benzene spectra. It consists of two terms

$$\Delta\nu = \nu_0 - \nu = nB + (n(3-n)/2 + 3p)C. \qquad (1)$$

Here ν_0 and ν are the 0,0 bands of benzene and the substituted benzene in wave numbers, n is the number of substituents, p is the number of pairs in para-position, and B and C are constants characteristic of the particular substituent. The number in the large bracket, called here μ, represents a geometrical property of the molecule. The same number is important for the intensity increase of the electronic transition in question over the intensity of the unsubstituted parent molecule, benzene, that is $I - I_0 = \mu A$. Here I_0 is the "vibrational" contribution to the intensity (taken as the benzene value), I is the total intensity and A is another constant characteristic of the substituent. The ratios of μ numbers in substituted benzenes $C_6H_5S : o\text{-}C_6H_4S_2 : m\text{-}C_6H_4S_2 : p\text{-}C_6H_4S_2 : 1,2,4\text{-}C_6H_3S_3 : 1,3,5\text{-}C_6H_3S_3 = 1:1:1:4:3:0$ correspond then roughly to the ratios of the observed intensities $I^{1b,1c,2}$ (f values). It was found possible to express the observed shifts in the spectra of the fluorinated benzenes by a Förster formula, if a negative value is chosen for B. The negative B might indicate the importance of the large electronegativity of the fluorine atom. The best fit of the fluoro-series is obtained for B values between -100 and -130 and corresponding C values between 380 and 410, all in wave numbers. The shifts of the corresponding chloroseries (all to the red) may be represented with B and C values of about 845 and 170 cm⁻¹, respectively. Because of scarcity of material in the fluoromethyl-series no similar representation is possible for the shifts in this

series and for the shifts in the fluorinated benzotrifluorides.

It is perhaps not superfluous to add to this discussion that all known near ultraviolet spectra of fluorinated benzenes in the vapor phase show discrete structure with sharp or rather sharp bands. The difference of appearance of the spectra of 1,3,5-trifluorobenzene and 1,3,5-trichlorobenzene is particularly striking.

TABLE I. Positions of 0,0 bands (vapor) and intensities in the near ultraviolet spectra of some fluorinated and chlorinated benzenes.

Molecule	0,0 band cm⁻¹	Intensity $f \times 10^2$
Benzene C_6H_6	38 089 calc	1.6
Fluorobenzene C_6H_5F	37 819[a]	8.9
m-difluorobenzene } $C_6H_4F_2$	37 909[b]	9.6
p-difluorobenzene }	36 943³	22.4
1,2,4-trifluorobenzene } $C_6H_3F_3$	37 123³	19.2
1,3,5-trifluorobenzene }	38 527³ calc	~2.0
1,2,4,5-tetrafluorobenzene $C_6H_2F_4$	36 605/12[e]	
Benzotrifluoride $C_6H_5CF_3$	37 819[d]	7.1
1,4-bis-trifluoromethylbenzene $C_6H_4(CF_3)_2$	37 460[e]	12.0
1,3,5-tris-trifluoromethylbenzene $C_6H_3(CF_3)_3$	~38 100³ calc	2.1
m-fluorobenzotrifluoride } $C_6H_4FCF_3$	37 355[e]	(14.7)
p-fluorobenzotrifluoride }	37 866[e]	(2.4)
2,5-difluorobenzotrifluoride $C_6H_3F_2CF_3$	36 800 sol[f]	27.0
Perfluorotoluene $C_6F_5CF_3$	37 700 sol[f]	21.0
Chlorobenzene C_6H_5Cl	37 052[g]	3.0
o-dichlorobenzene }	36 265[h]	4.0
m-dichlorobenzene } $C_6H_4Cl_2$	36 186[h]	4.1
p-dichlorobenzene }	35 743[h]	~6.8
1,2,4-trichlorobenzene } $C_6H_3Cl_3$	35 108[i]	~6.0
1,3,5-trichlorobenzene }	35 498[i] calc	2.1

[a] S. H. Wollman, J. Chem. Phys. 14, 123 (1946).
[b] V. Ramakrishna Rao and H. Sponer, Phys. Rev. 87, 213(A) (1952).
[c] Results of K. N. Rao in our laboratory.
[d] H. Sponer and D. S. Lowe, J. Opt. Soc. Am. 39, 840 (1949).
[e] W. T. Cave and H. W. Thompson, Disc. Faraday Soc. 9, 35 (1950).
[f] H. B. Klevens and Lois J. Zinning, J. chim. phys. 49, 377 (1952).
[g] H. Sponer and S. H. Wollman, J. Chem. Phys. 9, 816 (1941).
[h] H. Sponer, Revs. Modern Phys. 14, 224 (1942).
[i] Hedwig Kohn and H. Sponer, J. Opt. Soc. Am. 39, 75 (1949).

Solution Spectra and Oscillator Strengths of Electronic Transitions

of Pyridine and Some Monosubstituted Derivatives * †

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Abstract

The near ultraviolet absorption spectra of the following sub-
stances have been measured in isooctane and ethyl alcohol solutions:
pyridine, the isomeric picolines, 2- and 3-fluoropyridine, 2- and
3-chloropyridine, and 2- and 3-bromopyridine. Solvent effects were
observed and oscillator strengths were measured for the singlet-
singlet $\pi-\pi^*$ and $n-\pi^*$ electronic transitions which occur in the
spectral region 34,000 cm^{-1} to 48,000 cm^{-1}. It was found that in
this spectral region the $n-\pi^*$ transition is missing in the case
of 2-fluoro-, 2-chloro-, and 2-bromopyridine.

Introduction

The fact that in the near ultraviolet absorption spectra of pyridine, the diazines, and many of their derivatives there occur $n-\pi^*$ electronic transitions as well as $\pi-\pi^*$ transitions, makes it essential that criteria be available for distinguishing the two types. Two such criteria, which are proving particularly useful, are a comparison of solvent effects and a comparison of oscillator strengths (f values).[1] In the research reported here solvent effects have been observed and the oscillator strengths measured for the following substances: pyridine, and isomeric picolines, 2- and 3-fluoropyridine, 2- and 3-chloropyridine, and 2- and 3-bromopyridine. The solution spectra of all these compounds are known in the literature. Several of them, however, have been studied in only one solvent and without prior knowledge of the existence of the two types of electronic transitions. In order to make the oscillator strength determinations it was necessary, therefore, to make new measurements for all the substances.

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1 J.R. Platt, J. Chem. Phys. 19, 101 (1951).

Experimental

The spectrograms reported here in Fig. 1 through 10 were measured with a Beckman spectrophotometer using isooctane and 95 per cent ethyl alcohol solutions. The molar extinction coefficients ε were calculated from the equation

$$I = I_0 10^{-\varepsilon cl} , \qquad (1)$$

where c is the concentration in moles per liter and l is the path length in cm. Cells one cm long were used throughout this research.

The compounds were obtained from various sources. The pyridine was a commercial Merck product which had been purified by being distilled twice under ordinary pressure and then a third time after standing over potassium hydroxide. Dr. J.J. McGovern of the Mellon Institute supplied the samples of 2-picoline 99.85% pure (b.p. 129.44°) and 3-picoline 99% pure (b.p. 143.0-143.5°). The 4-picoline (b.p. 144.5-145.0°) was purified by Dr. J.C. Shivers of the Department of Chemistry, Duke University, and was purified further in this laboratory by an additional distillation.

Very pure samples of 2-chloropyridine, 2-bromopyridine, and 3-bromopyridine were obtained from Dr. M. Kasha. A few grams of 3-chloropyridine were synthesized and purified to special order by the Delta Chemical Works. Purity specifications were not available, but experiments with vapor absorption have indicated a high degree of purity. The samples of 2- and 3-fluoropyridine were given to us by Dr. Arthur Roe of the Department of Chemistry, the University of North Caroline. The samples had been very carefully dried and distilled and were supplied in vacuum-tight breakseals.

In the course of the research some difficulty with chemical decomposition arose for 2- and 3-bromopyridine and 2-fluoropyridine. The nature of the decomposition was rather imperfectly understood, but it

Table I

Comparison of Experimental Results with Literature

Compound	Band Maximum cm⁻¹	Maximum Molar Extinction	Solvent	Reference
Pyridine	39,750	2020	Isooctane	This research
	39,750	2040	Cyclohexane	2
	39,750	1630	Hexane	3
	39,750	2300	Heptane	4
	39,750	1970	Isooctane	5
	39,750	1770	Isooctane	6
	39,750	2070	Cyclohexane	7
	38,900	2630	Alcohol	This research.
	38,900	2240	Alcohol	8
	38,900	2600	Alcohol	9

2 F. Halverson and H.C. Hirt, J. Chem. Phys. 19, 711 (1951).

3 H. Fischer and P. Steiner, Compt. rend. 175, 882 (1922).

4 J.P. Wibaut and C.W.F. Spiers, Rec. des Trav. chim. des Pays-Bas 56, 573 (1937).

5 American Petroleum Institute Research Project 44 at the National Bureau of Standards. Catalog of Ultraviolet Spectrograms. Serial No. 34, Pyridine, contributed by the Union Oil Company of California.

6 API Research Project 44. Serial No. 108, Pyridine, contributed by the California Research Corporation.

7 E.F.G. Herington, Dis. Far. Soc. 9, 26 (1950).

8 Landolt-Börnstein Physikalisch-Chemische Tabellen. Berlin: Julius Springer, 1935. 5th edition, 3rd supplement, p. 1416.

9 W.K. Miller, S.B. Knight and A. Roe, J. Amer. Chem. Soc. 72, 1629 (1950).

Table I (continued)

2-Picoline	38,230	2420		
	39,000	2385	Isooctane	This research
	38,160	2430		
	38,900	2450	Isooctane	6
	38,160	2420		
	38,900	2530	Cyclohexane	10
	38,160	2700		
	38,900	2700	Cyclohexane	7
3-Picoline	38,750	2260	Isooctane	This research
	38.750	2250	Cyclohexane	7
4-Picoline	39,050	1550	Isooctane	This research.
	39,050	1600	Cyclohexane	7
2-Fluoro-pyridine	38.750	3200	Alcohol	This research.
	38.750	3250	Alcohol	9
3-Fluoro-pyridine	38.160	2990	Alcohol	This research.
	38.160	3050	Alcohol	9
2-Chloro-pyridine	37,800	2920	Isooctane	This research
	37,200	2750	Heptane	4
3-Chloro-pyridine	37,370	2400	Isooctane	This research
	37,900	2450	Heptane	4
2-Bromo-pyridine	37,580	2950	Isooctane	This research
	37,000	3000	Heptane	4
3-Bromo-pyridine	37,300	2270	Isooctane	This research
	37,500	2000	Heptane	4

[10] API Research Project 44. Serial No. 213, 2-Picoline, contributed by the Mellon Institute.

has appeared reasonably certain that the spectra were inappreciably affected thereby. A comparison with the literature, the major outline of which is given in Table I, shows that there is good agreement between the spectrograms reported in this research and those reported elsewhere. With regard to the difficulties with decomposition, it is significant that our data for the halogenated pyridines agree so well with the data of Wibaut and Spiers[4] published in 1937 and the more recent data of Miller, Knight and Roe.[9] The largest discrepancy was noted for 3-bromo-pyridine in non-polar solvents.

Solvent Effects

It has been largely due to the work of Kasha,[11] and Rush and Sponer[12, 13] that in pyridine the existence of at least one singlet-singlet $\pi-\pi^*$ electronic transition and at least one singlet-singlet $n-\pi^*$ electronic transition has been established. One of these transitions (referred to as Transition I) has its 0-0 band at $34,769$ cm^{-1} in the vapor and is now recognized[11, 12] as an $n-\pi^*$ transition. The second transition (referred to as Transition II) has its 0-0 band at about $38,350$ cm^{-1} in the vapor[13] and long remained undetected as a system independent of Transition I, because its bands are very diffuse and overlap Transition I around $38,500$ cm^{-1}.

Kasha first advanced the idea that in the diffuse region beginning at about $38,500$ cm^{-1} there is a strong $\pi-\pi^*$ transition (here called Transition II) and a somewhat weaker transition due to excitation of one of the nitrogen nonbonding $(2p^2)$ electrons ($n-\pi^*$ transition). He also came to the conclusion that Transition I is likewise an $n-\pi^*$ transition and not a $\pi-\pi^*$ transition as formerly supposed. According

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11 M. Kasha, Disc. Far. Soc. 9, 14 (1950).
12 J.H. Rush and H. Sponer, J. Chem Phys. 20, 1847 (1952). See this paper for many earlier references.
13 H. Sponer and J.H. Rush, J. Chem Phys. 17, 587 (1949).

to this view there would be three singlet-singlet transitions in the region 33,000 cm^{-1} to 48,000 cm^{-1} (see Fig. 1). Rush and Sponer definitely identified two of these transitions (Transitions I and II) in the vapor spectra of the isomeric picolines. The existence of the second n-π* system could not be definitely established from the vapor spectra studies.

It was upon interpretations of solvent effects that Kasha chiefly based his ideas. In this research the solvent effects which may be observed for Transition I have been investigated in considerable detail for pyridine and several derivatives. The essential features of the effects may be understood from Fig. 1 for pyridine. The 0-0 band positions as determined from vapor measurements are indicated with arrows. That the spectrograms taken in alcohol should be so much more discrete than that taken in isooctane solution has been the evidence given by Kasha for the existence of two transitions in the region of Transition II. Because of the lack of supporting evidence from vapor spectra, the evidence must be considered to be inconclusive at the present time. The situation is much more satisfactory with regart to Transition I.

From the spectrograms one can see that in the region of Transition I (about 34,000 cm^{-1} to 37,500 cm^{-1}) the intensity of pyridine absorption decreases in alcohol solution as compared to that in isooctane solution. The intensity decrease may be interpreted by the assumption that in alcohol the nitrogen nonbonding sp^2 electrons become involved in the formation of a hydrogen bond, and that consequently their excitation required more energy and thus the n-π* transition moves towards the violet. An assumed hydrogen bond strength of about 6 kcal/mole might be expected to correspong to a shift of about 2000 cm^{-1}. Such

a shift would be sufficient to cause Transition I to move well into the region of Transition II and hence to be obscured by the latter transition.

In accordance with the results of Rush and Sponer that all three of the picolines possess a Transition I and a Transition II, one sees from Fig. 2,3, and 4 that the effect of the two solvents upon the spectrograms of the picolines is the same as for pyridine, that is, the region of Transition I decreases in intensity when the change is made from isooctane to alcohol while the region of Transition II increases in intensity. The spectrograms of 3-fluoropyridine, 3-chloropyridine, and 3-bromopyridine shown in Figs. 6,8, and 10 reveal that those substances also react to a solvent change in exactly the same way as pyridine. The vapor spectra of these substances have also been measured in this laboratory, and the existence of the two transitions for those compounds has been definitely established.

The situation is very different, however, for 2-fluoropyridine, 2-chloropyridine, and 2-bromopyridine. Figs. 5,7, and 9 show that these substances do not react to a solvent change in the same way as does pyridine. In the low-energy regions of the spectrograms the strength of absorption is practically the same in alcohol solution as in isooctane solution. It appears as though the solvent effect criterium for assigning Transition I as a nonbonding electron transition has no validity for these ortho-substituted compounds. Vapor spectra studies made in this laboratory have shown, however, that these substances actually do not have a singlet-singlet $n-\pi^*$ transition in the spectral regions explored by these experiments. It will be made clear later how this fact may be interpreted so as to add weight to the argument that Transition I is an $n-\pi^*$ transition.
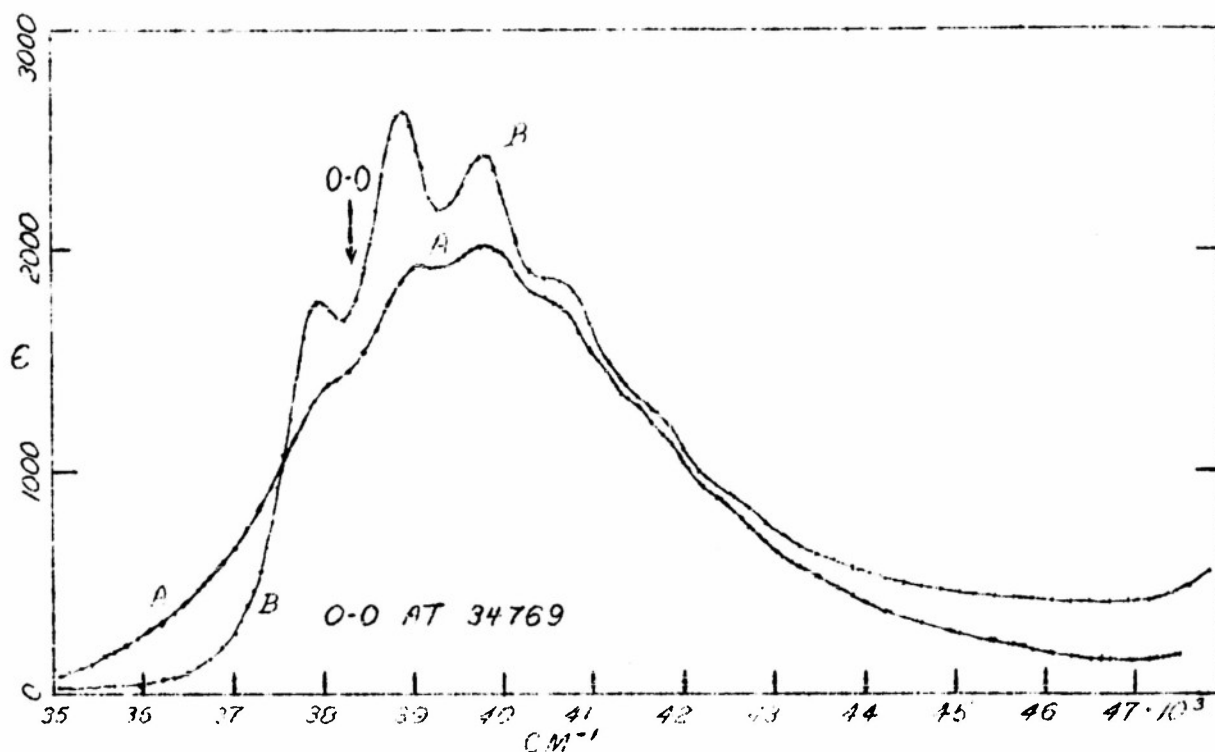
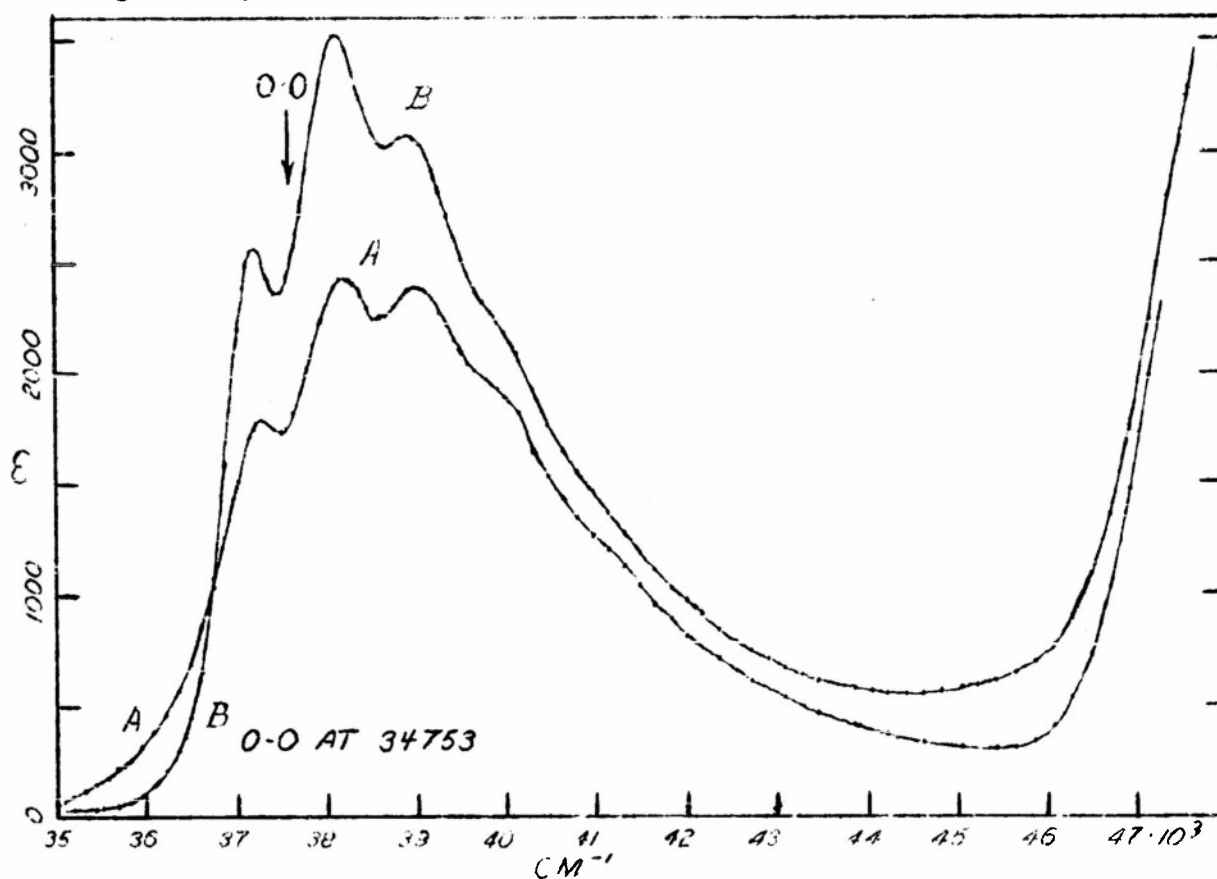Fig. 1. Pyridine in (A) Isooctane, (B) 95% Ethyl Alcohol.

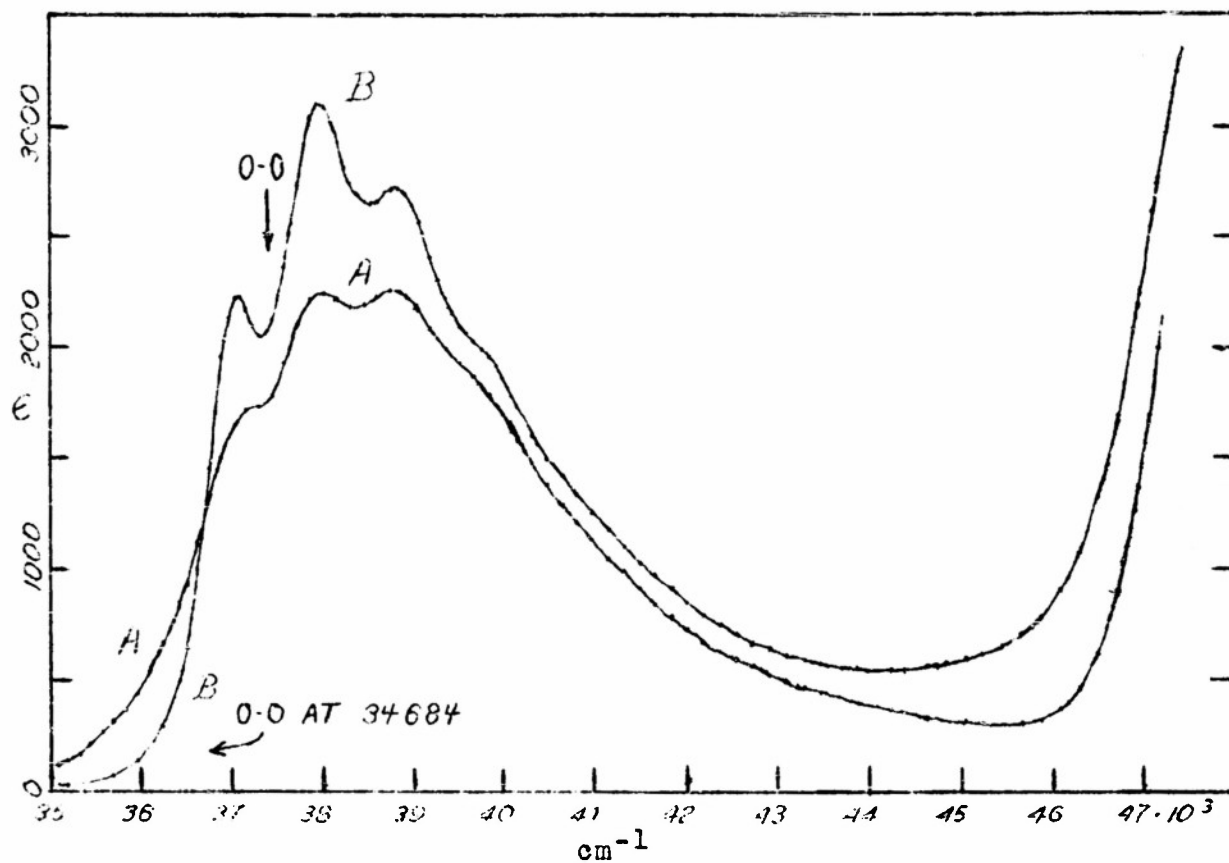Fig. 2. 2-Picoline in (A) Isooctane, (B) 95% Ethyl Alcohol.

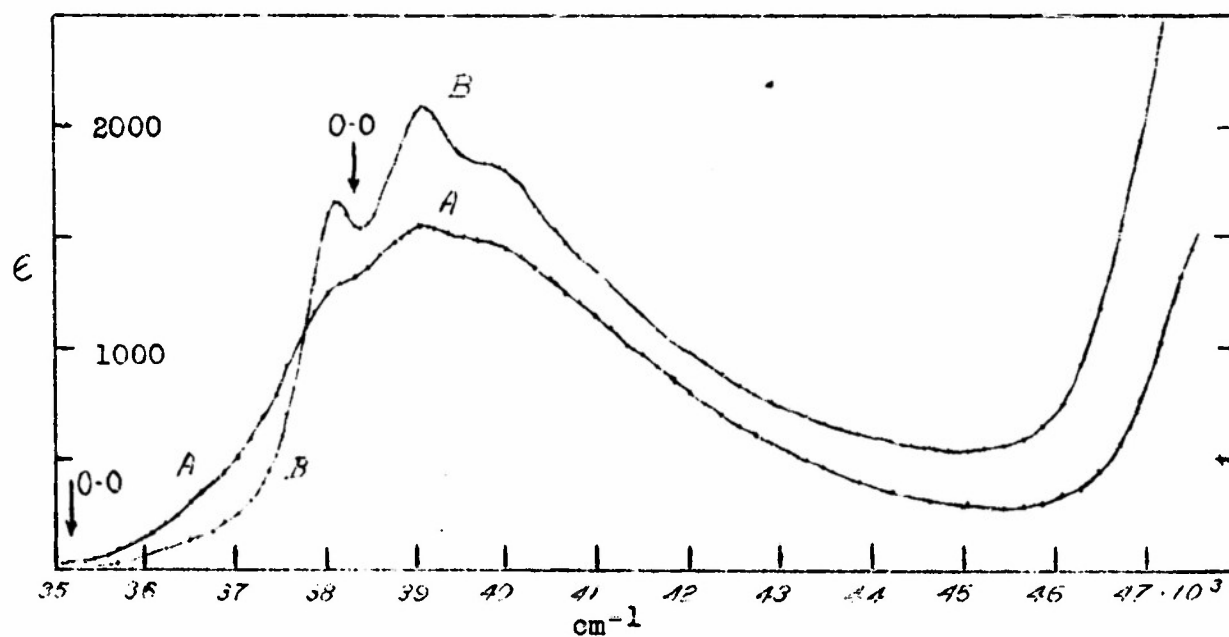Fig. 3. 3-Picoline in (A) Isooctane, (B) 95% Ethyl Alcohol.

Fig. 4. 4-Picoline in (A) Isooctane, (B) 95% Ethyl Alcohol.

Fig. 5. 2-Fluoropyridine in (A) Isooctane, (B) 95% Ethyl Alcohol.

Fig. 6. 3-Fluoropyridine in (A) Isooctane, (B) 95% Ethyl Alcohol.

Fig. 7. 2-Chloropyridine in (A) Isooctane, (B) 95% Ethyl Alcohol.
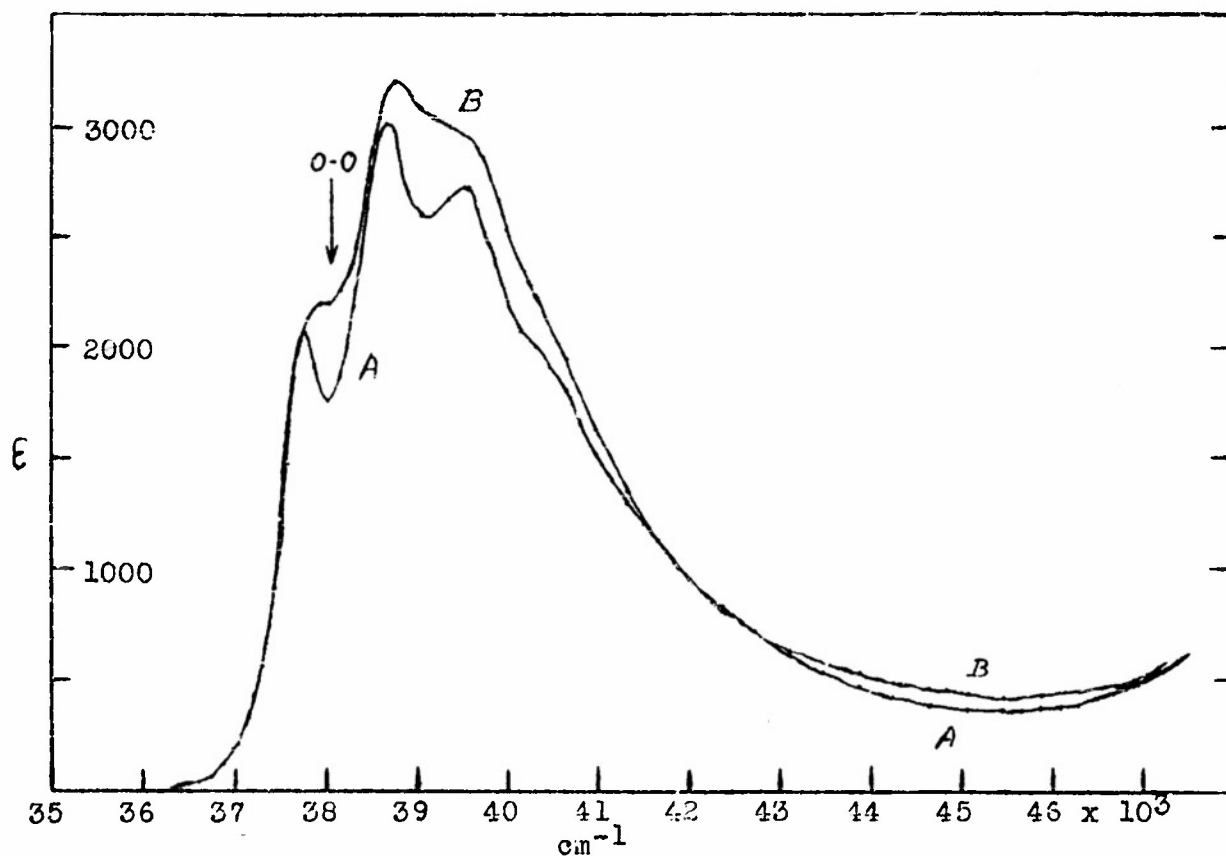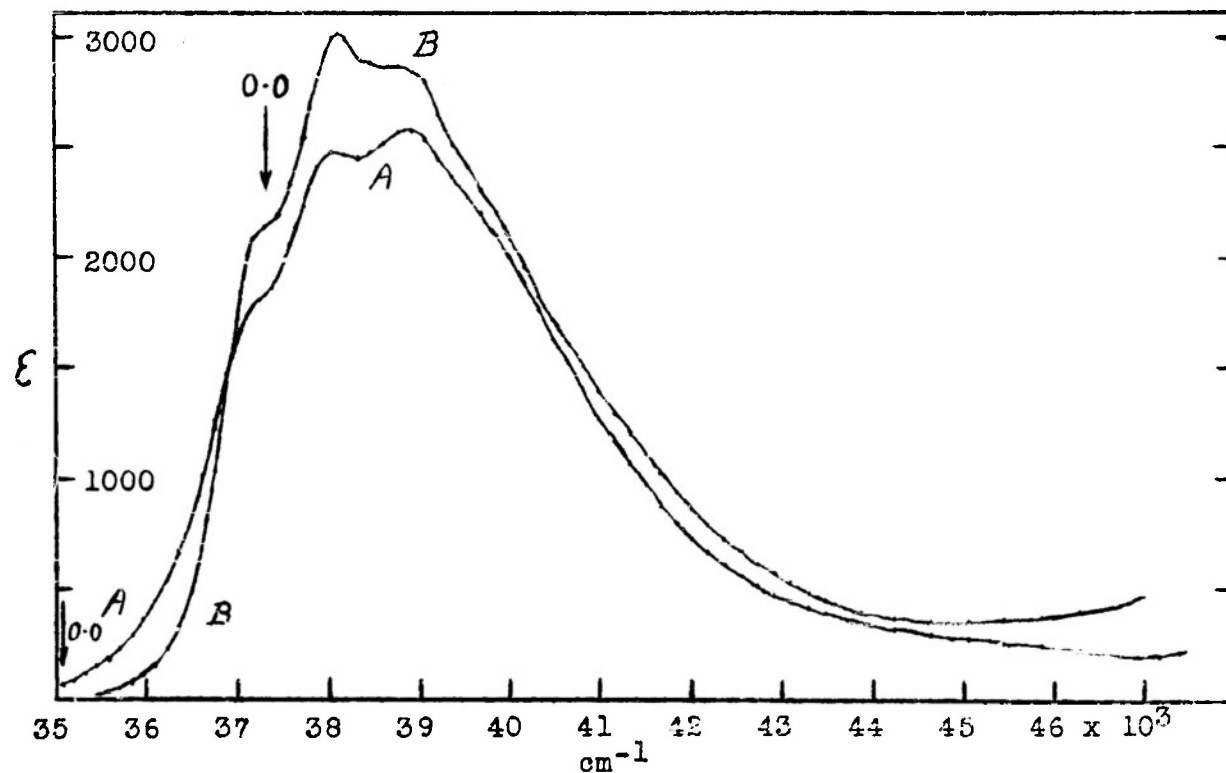

Fig. 8. 3-Chloropyridine in (A) Isooctane, (B) 95% Ethyl Alcohol.

Fig. 9. 2-Bromopyridine in (A) isooctane, (B) 95% Ethyl Alcohol.
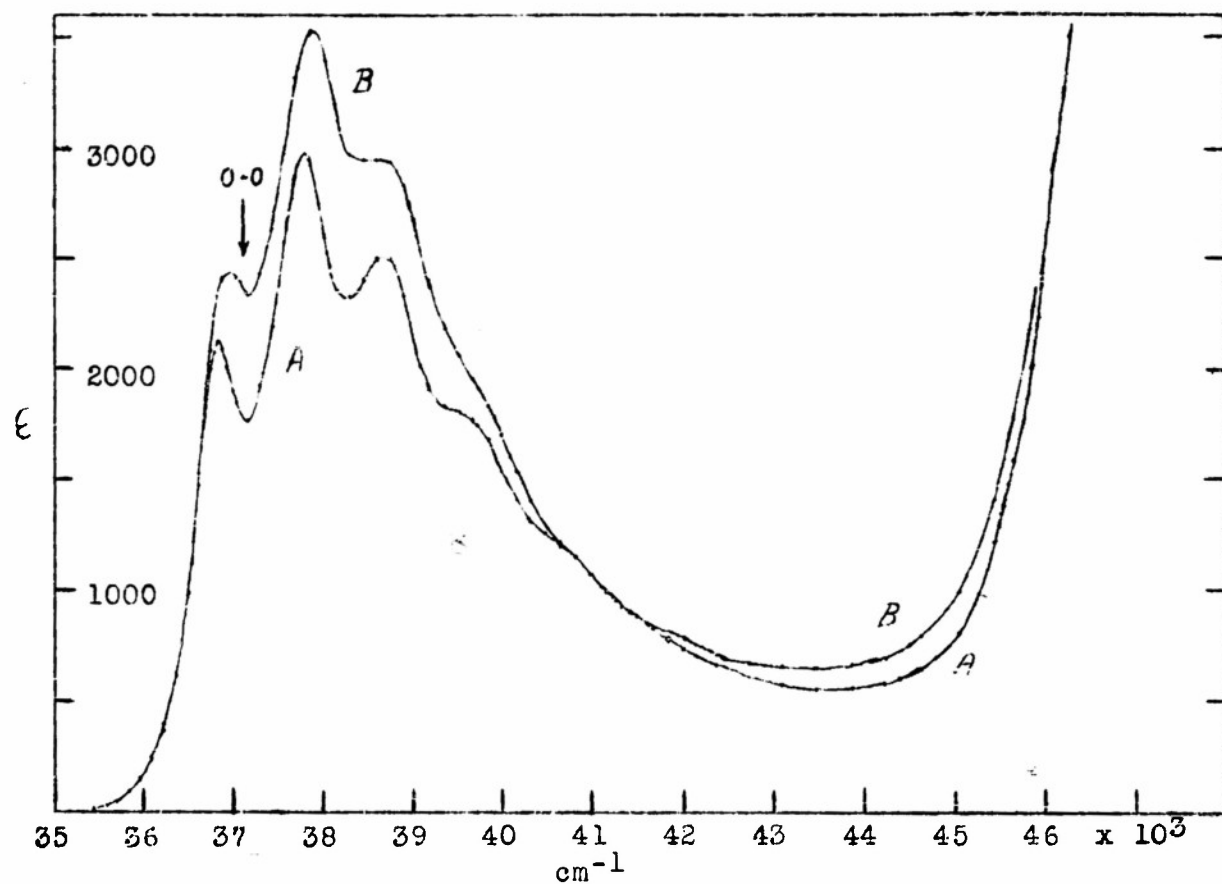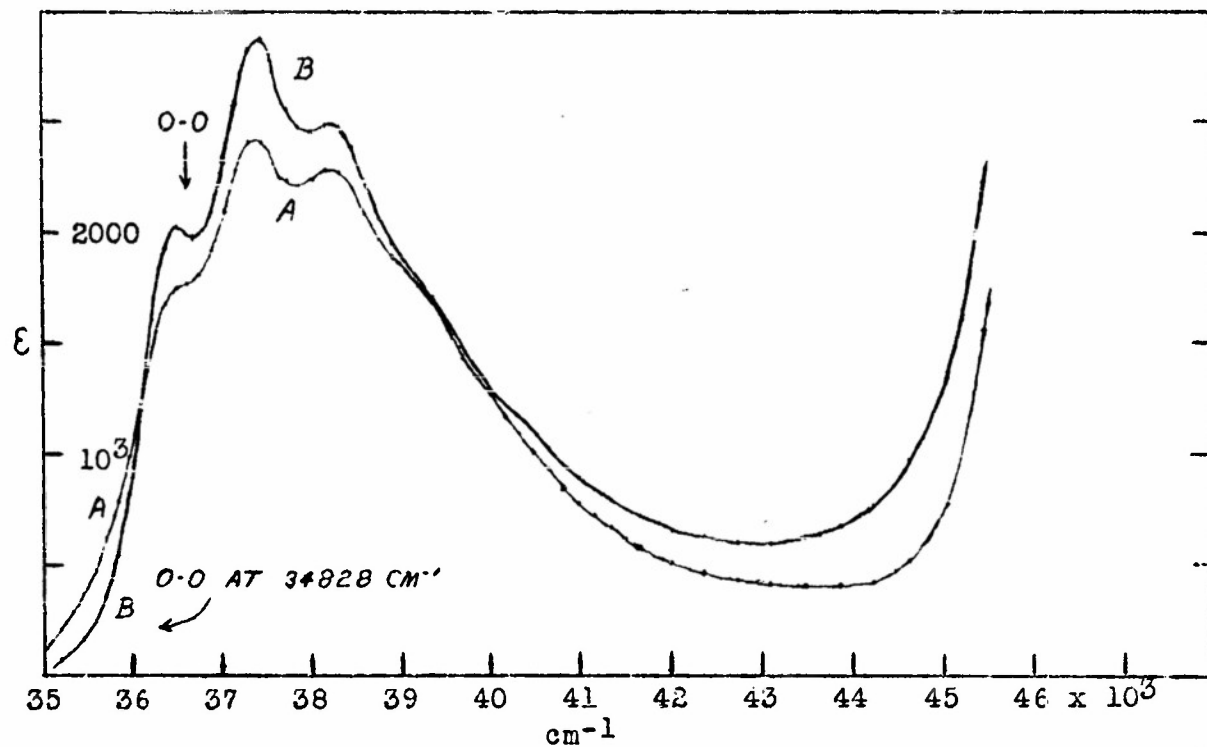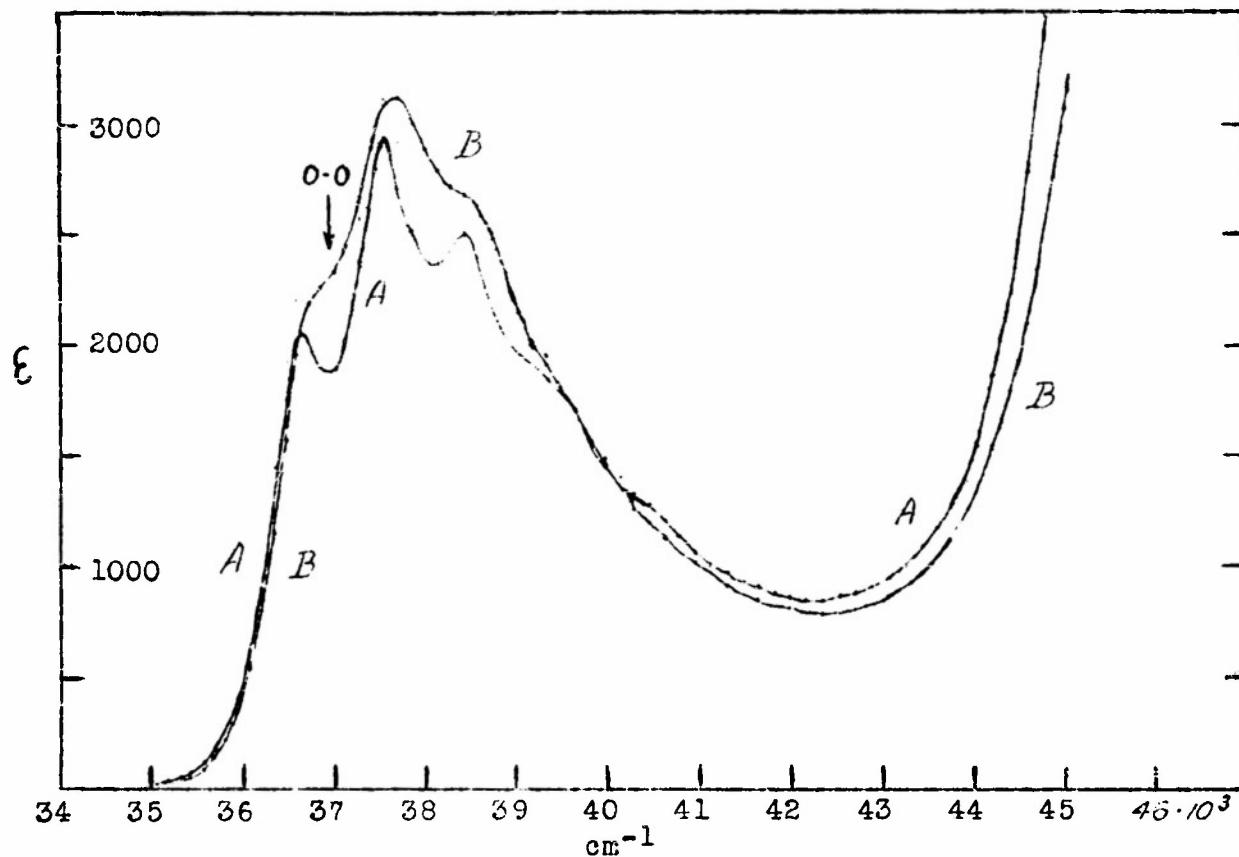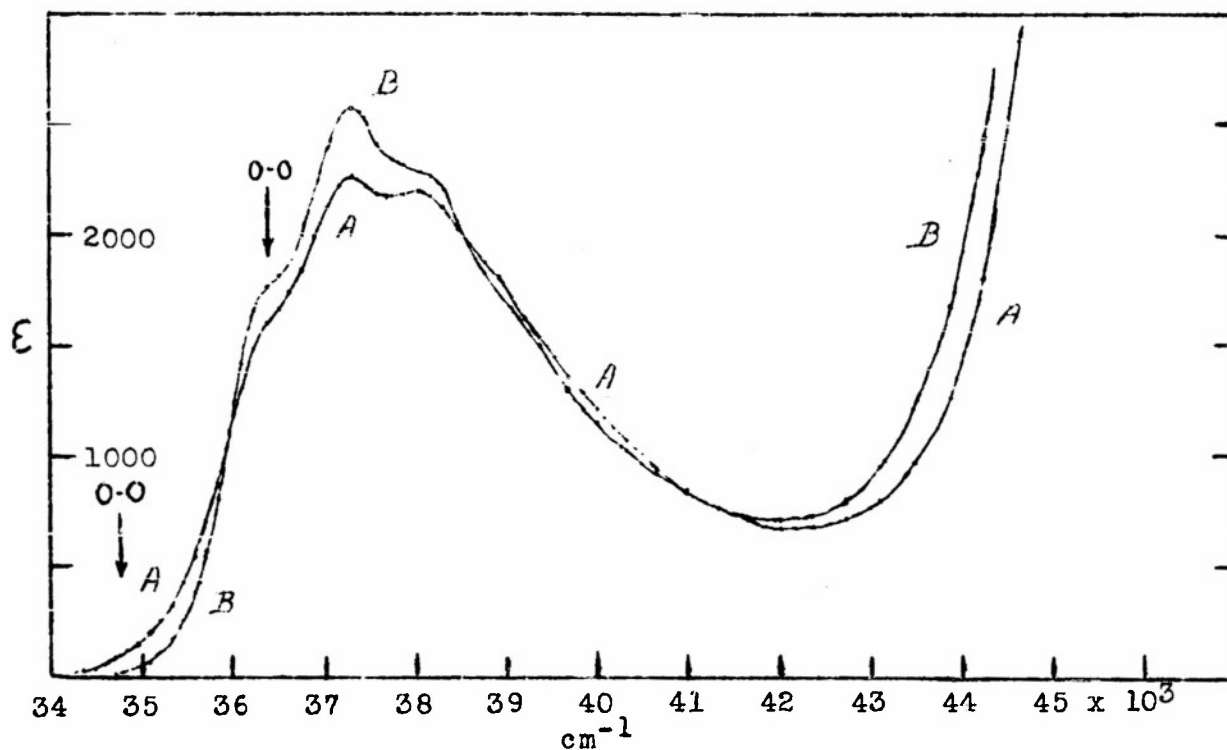

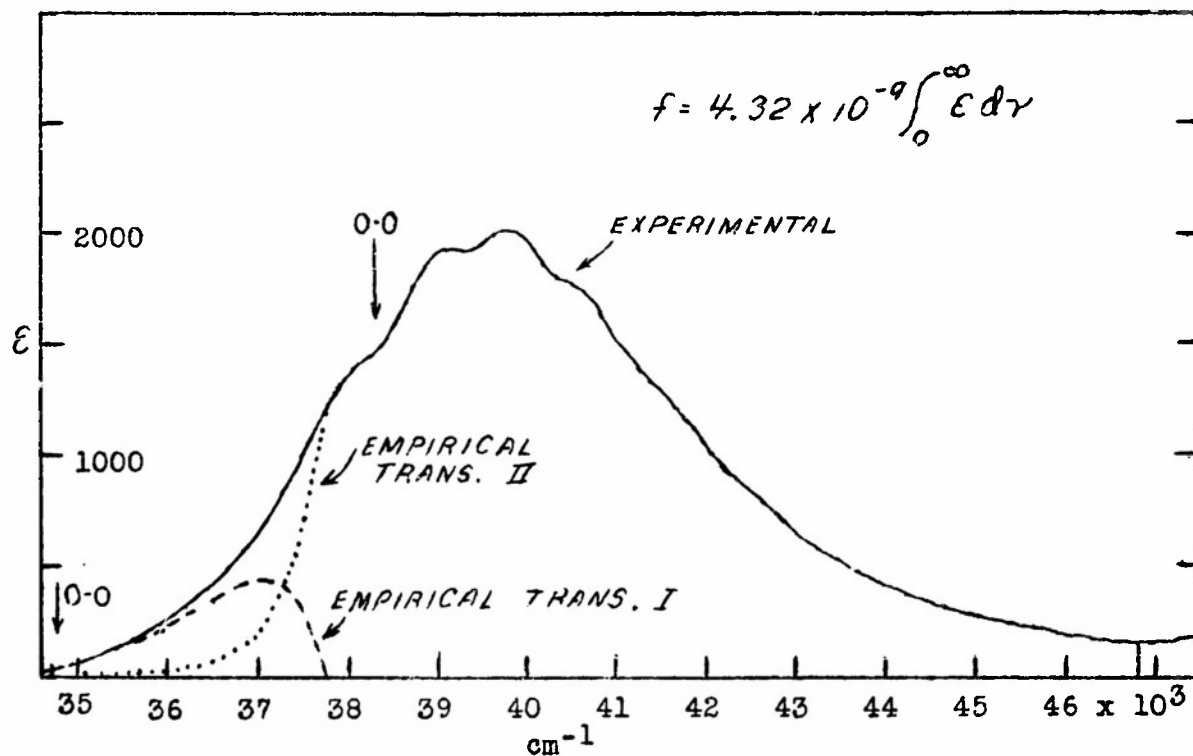Fig. 10. 3-Bromopyridine in (A) Isooctane, (B) 95% Ethyl Alcohol.

$$f = 4.32 \times 10^{-9} \int_0^\infty \mathcal{E}\, d\gamma$$

Fig. 11. Pyridine in Isooctane. Illustration of Empirical Constructions and Area Measurements.

Determination of Oscillator Strengths

From Figs. 1 through 10 it can be seen that Transitions I and II are very close together in the spectrograms in which they appear as identifiable transitions and are furthermore not separated by a minimum. However, from the following considerations it is possible to arrive at a separation of the two absorbing regions. For all the spectrograms, even if there is no Transition I, the absorption intensity in the region of Transition II increases when the solution change from isooctane to alcohol is made. If we assume the extreme case that it is mainly Transition II whose intensity is increased in alcohol and that Transition I is negligibly weak when it is shifted into the second region, we may construct separated curves for isooctane solution in the following way:

Let the first principal maximum at 38,000 cm^{-1} (Fig. 1) be chosen to represent a measure of the relative intensity increase of Transition II in alcohol. The increase is 20 percent (from 1370 to 1765). If now the entire portion of the curve in alcohol solution from this maximum toward smaller wavenumbers is diminished by 20 per cent and the derived curve portion is joined at 38,000 cm^{-1} with the experimental curve in isooctane, a spectrogram for Transition II in isooctane is obtained which might be measured if Transition I were entirely missing. This empirical spectrogram is shown in Fig. 11. When the ordinates, from the connecting point to lower wavenumbers, of the experimental and the derived isooctane spectrograms are subtracted from one another, absolute ordinate values for Transition I are obtained, and these have been plotted in Fig. 11 in dashed outline.

On the other hand, if it is assumed that the increase in absorption of the alcohol solution spectrogram in the region from 38,000 cm^{-1} to

larger wavenumbers is entirely due to the shifted Transition I, then
the oblong area between the isooctane curve (curve A) and the alcohol
curve (curve B) from 34,000 cm^{-1} to 37,500 cm^{-1} in Fig. 1 should be
equal in magnitude to the portion of the curve B over curve A between
37,500 cm^{-1} and 41,000 cm^{-1}. It may be seen that the two areas are
approximately in the ratio 2:3. This would mean that only 1/3 of the
intensity increase must stem from a solution effect on Transition II.
Consequently, the low energy part of curve B should be corrected by only
1/3 of 20 percent, that is by 7 percent, and the dashed area of Tran-
sition I would be correspondingly smaller. The best approximate values
would lie between these two extreme cases. Since the whole variation
is small and since not more than the correct order of magnitude may be
expected, the f values given in Table II have been obtained by using
the method giving the maximum correction. Although the procedure is
probably good enough for an approximate separation of the transitions,
it should not be forgotten that what here has been called Transition II
might consist of a $\pi-\pi^*$ and an $n-\pi^*$ transition as mentioned before.
This fact would introduce a complication into the treatment of this
region.

According to the well-known equation

$$f = 4.32 \times 10^{-9} \int_0^\infty \varepsilon \, dv \qquad , \qquad (2)$$

the oscillator strength of an electronic transition is proportional to
the area under the absorption curve. In the case of pyridine, there-
fore, the oscillator strengths of Transitions I and II may be immediate-
ly determined from the areas enclosed by the curves of Fig. 11. In this
research the actual measurements were made with a polar planimeter from
drawing-board size graph paper, the constructions for all the substances
being similar to that for pyridine. For Transition II a special element
of arbitrariness arises in the area measurement, because at no place on

the high wavenumber side of the spectrograms does the value of $\mathcal{E}$ drop to zero. It was assumed that in the region around 46,000 - 48,000 cm^{-1} Transition II and the next strong transition further to the violet overlap one another symmetrically about the point of minimum absorption. At this point (see Fig. 11) a vertical line was used to define the edge of the measured area. The results of all the f value determinations are given in Table II, where all the numbers have been rounded off to two significant figures.

Table II
Oscillator Strengths (f values)

Compound	Solution in Isooctane		Solution in Ethyl Alcohol
	Transition I $n-\pi^*$	Transition II $\pi-\pi^*$	Transition II $\pi-\pi^*$
Pyridine	0.0030	0.041	0.049
2-Picoline	19	47	59
3-Picoline	22	45	53
4-Picoline	23	32	40
2-Fluoropyridine	--	49	54
3-Fluoropyridine	22	49	55
2-Chloropyridine	--	48	55
3-Chloropyridine	14	44	48
2-Brompyridine	--	47	50
3-Bromopyridine	095	42	43

Discussion

Sklar,[14] in his study of the intensities of π-electron transitions
in substituted benzenes, has shown that when two substituents are both
either ortho-para-directing or meta-directing, first-order addition of
"migrational moments" may be made according to the following theorem:
the transition (migrational) moment due to a second radical in the po-
sition ζ is rotated from that of a radical in position γ by an angle
$\mathcal{T} = (\zeta \ 0 \ \gamma)$ and multiplied by $(-1)\frac{3\mathcal{T}}{\pi}$. The separate vector moments
need not be of the same magnitude. When the substituents are dissimilar
in their ring-directing property, the vector addition is governed by
the theorem that the migration moment due to a meta-directing group is
180° out of phase from that which would be produced by an ortho-para-
directing group in the same ring position. Sklar presented empirical
evidence which justified the omission of induction and vibration effects
in the calculations and assumed the intensity of the electronic transi-
tions to be proportional to the square of the migrational moments alone.

Sklar's theoretical predictions checked very well with data on the
near ultraviolet absorption spectra of benzene derivatives for which it
could be assumed that the ring perturbations were not too strong and no
new transitions were introduced by the substituents (methyl benzenes,
for example). It is interesting, therefore, under the assumption that
the nitrogen in pyridine acts as a meta-directing substituent, that the
f values reported here for pyridine and the picolines check rather well
with the Sklar theory in the case of Transition II. Disregarding factor
of proportionality, the transition moment diagrams for pyridine and the
picolines would be shown in Fig. 12. The phase for the diagrams have

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[14] A.L. Sklar, J. Chem. Phys. 10, 135 (1942) and Rev. Modern Phys.
14, 232 (1942).

been chosen so that the transition moment of the first substituent
(meta-directing N atom) points along the negative x axis. One sees
immediately that 2- and 3-picoline should have the same f values.
Using pyridine and 4-picoline as the "standards", the calculated f
value for 2- and 3-picoline is 0.046. This result is in excellent
agreement with the experimental values of 0.047 and 0.045 (see Table
II).

From Table II one can conjecture that the same good agreement
with Sklar's theory would exist for the halogenated pyridines if
measurements on the unstable para-derivatives could be made. It
is important to point out, however, that for the picolines and all
the halogenated pyridines, except the fluorine compounds, the
ortho-substituted substances possess a slightly higher f value than
the meta-substituted ones. This systematic difference is not
taken care of by the Sklar theory. That the fluorinated pyridines
have the largest f values is in accord with corresponding results
for fluorinated benzenes.[15]

In contrast to Transition II, the intensity distribution of
Transition I in pyridine and the picolines can not be adapted to
the predictions of the Sklar theory. This failure of agreement
is in accord with the view that the transition is not due to π-
electrons but rather to the nitrogen nonbonding electrons. The
fact that the various Transitions I have oscillator strengths of
the same order of magnitude as the forbidden 2600 $\overset{o}{A}$ transition
in benzene ($f \sim 10^{-3}$) was the reason for a suggestion by Kasha
that these transitions are forbidden ones. However, the analysis
of the vapor spectra[12] has shown that the Transitions I are not
forbidden by symmetry as is the case for benzene where a weak

15 H. Sponer, J. Chem. Phys., in press.

transition occurs due to the interaction of an antisymmetric vibration of particular symmetry. From symmetry arguments it follows that the polarization vector is perpendicular to the plane of the ring and is rather small since the excited orbital has a node where the ground state orbital has a maximum. An additional reason for the weakness is that the excited electron must move from an orbital localized on the nitrogen atom into a non-localized orbital distributed over the entire molecule ("spatial" forbiddenness, Platt).[1]

Special Behaviour of Ortho-halogenated Pyridines

It is significant that the disappearance of Transition I in the ortho-halogenated pyridines is not an isolated phenomenon. A number of years ago Uber[16] and Uber and Winters[17] studied the near ultraviolet absorption spectra of pyrimidine (1,3-diazine) and several chloropyrimidines both in the vapor state and in solution, and they found that some 125 sharp, line-like bands which appear with pyrimidine in the 2700-3300 Å region disappear entirely with dichloropyrimidine. Halverson and Hirt[2] have extended the work of Uber and Winters to include a study of the chlorinated pyrazines (1,4-diazine) and rather less completely a study of the corresponding pyridizines (1,2-diazine). In pyrazine, they identified an $n-\pi^*$ transition at 31,000 cm^{-1} and found that the 0-0 band shifted towards the violet by 1700 cm^{-1} with 2-chloropyrazine, by 3200 cm^{-1} with 2,3-chloropyrazine, and by comparable amounts for several other chloropyrazines. Thus,

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16 F.M. Uber, J. Chem. Phys. 9, 777 (1941).

17 F.M. Uber and R. Winters, J. Amer. Chem. Soc. 63, 137 (1941).

with this series of compounds the violet shift could be followed
step by step.

Since the excited π^* orbital in the pyrazines probably de-
creases in energy upon the chlorine substitution, the localized
orbital of the nitrogen nonbonding electrons must then correspond
in energy to a firmer binding in order to account for the violet
shift of the n-π^* transition. A general lack of ionization po-
tential and dissociation constant data does not permit one to
check independently that in these halogenated heterocyclics the
nonbonding electrons are more firmly bound than in the parent
molecule, but the strongly inductive character of halogen atoms
makes the assumption of increased binding energy very plausible,
particularly if the halogen atom is located very near the nitrogen
atom. With respect to the results of this research, it can be
conjectured, therefore, that Transition I is "missing" for 2-
fluoro-, 2-chloro-, and 2-bromopyridine simply because the in-
ductive attraction of the halogen atoms attached to the carbon
atom adjacent to the nitrogen atom increases the binding energy
of the nonbonding electrons over that existing in pyridine. It
is assumed that the increase in energy is such that the n-π^*
transition shifts into the spectral region of the π^* tran-
sition or further.

With regard to 3-fluoro-, 3-chloro-, and 3-bromopyridine,
data secured in this laboratory from vapor-state measurements
indicate, if one assumes a constant variation for the energy of
the excited state, that the term value of the nonbonding orbital
progressively increases as the electronegativity of the halogen
atom increases. The increase in binding energy, is however, in

these cases never large enough to cause Transition I to shift
completely into the region of Transition II (see Figs. 6,8, and
10). This situation is undoubtedly due to the meta-location of
the halogen atoms.

ION OF NITROBENZENE*

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Acknowledgements

ON THE ABSORPTION OF NITROBENZENE[*]

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ABSTRACT

The 2500 $\overset{o}{A}$ transition of nitrobenzene is interpreted as a superposition of a strong and a weak transition corresponding to the 2100 $\overset{o}{A}$ and 2600 $\overset{o}{A}$ transitions of benzene. The very weak transition of nitrobenzene near 3500 $\overset{o}{A}$ is considered to be related to the NO_2 group. Evidence supporting this interpretation is given.

INTRODUCTION

The absorption curve of nitrobenzene in solution shows a strong transition without any structure at 2500 Å (40,000 cm^{-1}), ϵ_{max} = 8500.[1,2] Another transition, which is much weaker, has been observed at 3500 Å (28,600 cm^{-1}), $\epsilon_{max} \approx$ 100.[1,3] In the region of 2900 Å (34,500 cm^{-1}) one of the published nitrobenzene curves shows a very slight inflection, which possibly indicates the existence of a third transition.[1] Various interpretations have been given for these transitions.[1,4] Recently it has been assumed[2] that the great intensity of the 2500 Å transition is due to resonance of the NO_2 group with the benzene ring whereby supposedly either the weak 2600 Å transition of benzene (referred to hereafter as transition I) or a "nitroband" is intensified. In the following pages a different interpretation of this transition will be given. It is assumed to correspond to the 2100 Å transition of benzene, referred to hereafter as transition II, and the supposed 2900 Å transition is interpreted as corresponding to transition I of benzene. The weak transition at 3500 Å is considered to be related to the NO_2 group. This interpretation assumes that substitution of NO_2 in benzene has the same effect on the absorption spectrum of benzene as substitution by other groups. It is known that the entry of a substituent into the benzene ring

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[1] K. L. Wolf and W. Herold, Z. Physik. Chem. B 13, 201, (1931); see also Landolt-Börnstein I (1951); Atom-und molekularphysik, 3. Teil, p. 267.
[2] W. G. Brown and H. Reagan, J. Am. Chem. Soc. 69, 1032 (1947).
[3] G. Scheibe, Ber. 59, 2617 (1926).
[4] G. Kortüm, Z. phys. Chem., B 42, 39 (1939).

moves transitions I and II towards the red, in some cases slightly, in others to a considerable extent. We assume here that NO_2 substitution is no exception to this rule and that transition II shifts so far that it covers transition I.

EVIDENCE FOR THE SUGGESTED INTERPRETATION
OF THE NITROBENZENE SPECTRUM

Evidence for the new interpretation may be found from a comparison of the absorption curve of nitrobenzene with the well-known curves of

(a) The nitrotoluenes,[2,5] dinitrobenzenes,[4,6,7] and chloro-nitrobenzenes.[1,8]

(b) β-nitronaphthalene.[9,10]

(c) m-nitro-nitrosobenzene.[7]

(a) The absorption curves of the nitrotoluenes, dinitrobenzenes and chloro-nitrobenzenes. In this section we shall first present some evidence that the nitrobenzene curve very probably has a hidden transition near 2900 Å, and for this

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[5] L. Dede and A. Rosenberg, Ber. 67, 147 (1934).
[6] P. Fielding and R. W. Le Fèvre, J. Chem. Soc. (1950), p. 2812.
[7] H. Nakamoto, Bull. Chem. Soc. Jap. 25, 255 (1952).
[8] G. Förster and J. Wagner, Z. physik. Chem. B35, 343 (1937).
[9] E. Hertel, Ztschr. Elektrochemie 47, 814 (1941).
[10] H. H. Hodgson and D. E. Hathway, Trans. Faraday Soc. 41, 115 (1945).

purpose the known curves of the nitrotoluenes, dinitrobenzenes
and chloro-nitrobenzenes will be used. Three isomers of each
compound are known. The meta compounds are the most suitable for
our purposes and will be used for comparison, although the o-
compounds give similar results. The absorption curves of all
three meta compounds resemble the nitrobenzene curve. All show
a maximum absorption peak near 2500 $\overset{o}{A}$, $\varepsilon_{max} \sim 8000$ (m-dinitro-
benzene shows in alcohol a distinct inflection at 2600 $\overset{o}{A}$ [6]). All
these compounds have, like nitrobenzene, a weak transition
($\varepsilon_{max} \sim 100$) near 3500 $\overset{o}{A}$. The very slight inflection of the
nitrobenzene curve near 2900 $\overset{o}{A}$, which most published nitrobenzene
curves do not show at all, is distinctly revealed in m-nitro-
toluene and in m-dinitrobenzene at about the same location. m-
Chloro-nitrobenzene shows even a well separated transition near
3000 $\overset{o}{A}$. These facts make the presence of a hidden transition
near 2900 $\overset{o}{A}$ in nitrobenzene very probable. Kortüm[4] who investi-
gated the absorption curves of the nitrotoluenes, the dinitro-
benzenes and of s-trinitrobenzene in water, came to the same con-
clusion as far as the existence of a hidden transition in nitro-
benzene is concerned, but gave an interpretation of the nitro-
benzene transitions which differs from the one presented here.

Ortho-nitrotoluene reveals the hidden transition even more
distinctly than the corresponding m-compound, but the intensity
of the 2500 $\overset{o}{A}$ transition is decreased in the o-compound. The same
intensity decrease is shown by o-chloro-nitrobenzene.

The p-compounds are not suited for our purpose, as in these
compounds the two transitions lie apparently so close together
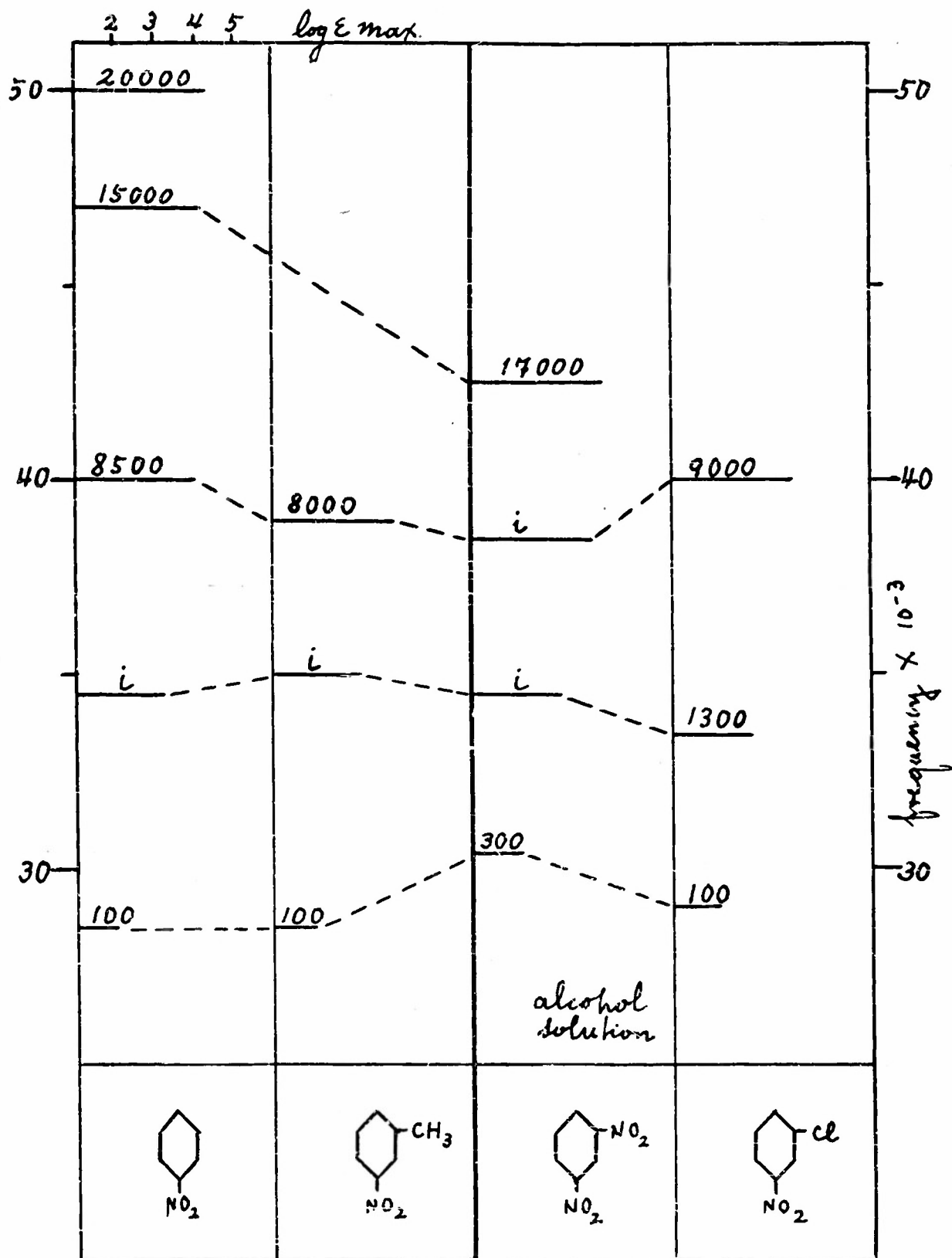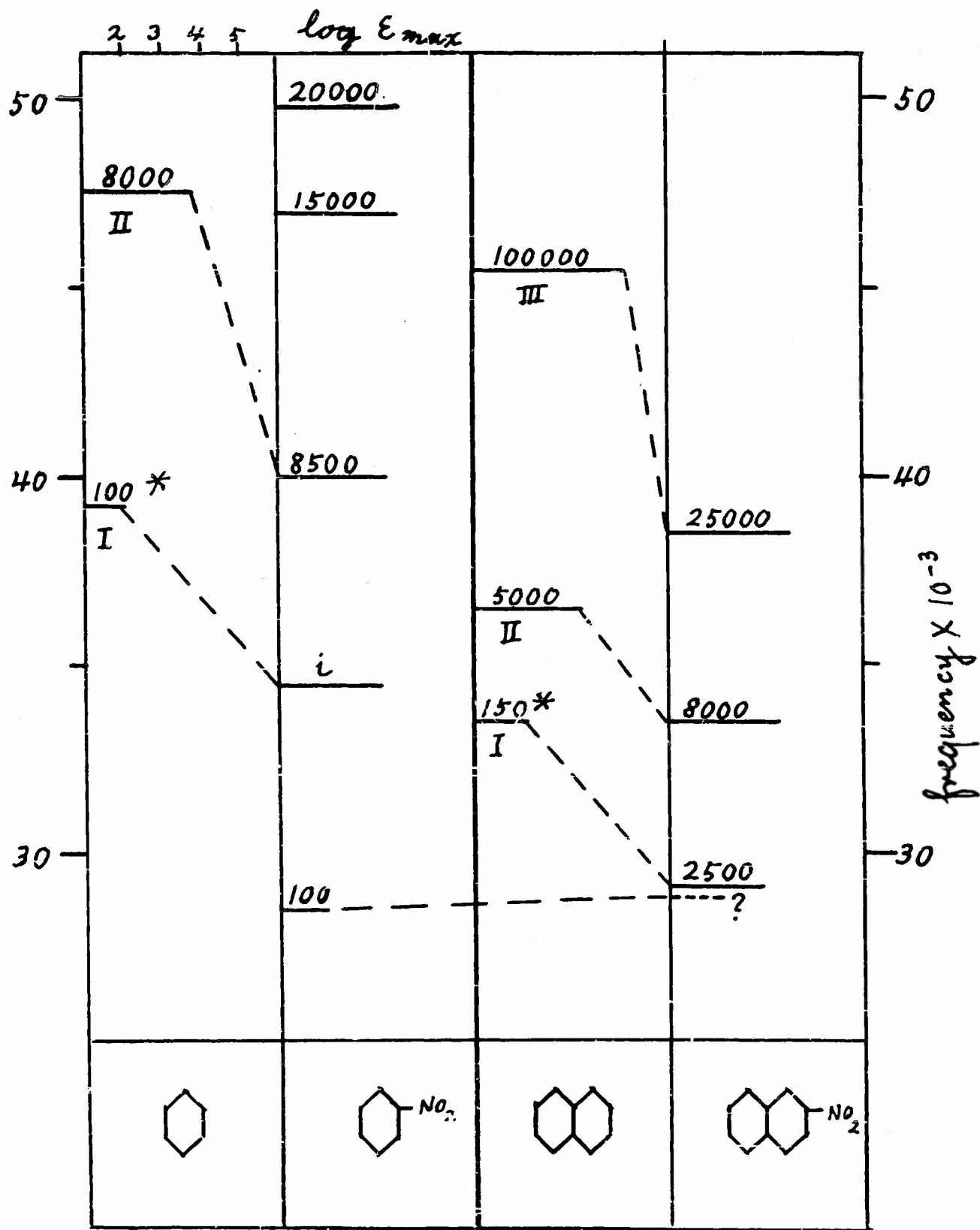
that the weaker transition is completely masked.[8]

A clue to the intensity of the hidden 2900 $\overset{o}{A}$ transition of nitrobenzene can best be obtained from the corresponding transition of m-chloro-nitrobenzene. Only in this substance is the weaker transition well separated from the strong 2500 $\overset{o}{A}$ transition. Its intensity is $\mathcal{E}_{max} \sim 1300$ in hexane. The hidden transition of nitrobenzene may therefore be expected to have a similar intensity.

Figure 1

Spectra of meta derivatives of nitrobenzene, all in nonpolar solvents with the exception of m-dinitrobenzene. Number above horizontal bars indicates $\mathcal{E}_{max}$. i indicates inflection.

Figure 2

Nitrosubstitution in benzene and naphthalene, nonpolar solvents.* $\mathcal{E}$ is $\mathcal{E}_{sm}$ from ref. 11.

(b) The absorption curve of β-nitronaphthalene. We have so far made plausible that in the nitrobenzene spectrum a hidden transition is very probably present near 2900 $\overset{o}{A}$. We now wish to present evidence that this hidden transition may correspond to transition I of benzene and that the strong 2500 $\overset{o}{A}$ transition

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[11] J. R. Platt, J. Chem. Phys. 19, 263 (1951).

masking the 2900 Å transition may correspond to transition II of benzene; in other words, that NO_2 substitution has the same effect on the benzene spectrum as other substituents have. Our reasoning is based on the spectral resemblance of the cata-condensed hydrocarbons as outlined by Platt,[12] and on the fact that certain regularities become apparent when the spectra of benzene and naphthalene derivatives are compared.[13] Introduction of the same substituent in benzene or naphthalene (β-substitution) produces, expressed in wave numbers, approximately the same shift of transition I in both cases. However, the effect of substitution on transition II is different. Substituents, which in benzene cause a strong shift of transition II towards the red, shift transition II of naphthalene only slightly and do not change its intensity much. It is further known that transitions I of corresponding benzene and naphthalene derivatives have similar intensities.* If NO_2 substitution has the same effect as these other substituents, then it should be possible to predict from the available data of the nitrobenzene curve the shape of the β-nitronaphthalene curve. NO_2 substitution, according to our interpretation, produces in benzene a shift of transition I of about 4700 cm^{-1}. Approximately the same shift is caused by NH_2-substitution.[14]

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*These regularities occur for ortho-para directing as well as for meta directing substituents. See also W. F. Hamner and F. A. Matsen, J. Am. Chem. Soc. 70, 2482 (1948).

[12] J. R. Platt, J. Chem. Phys. 17, 470 (1949).
[13] H. G. de Laszlo, Proc. Roy. Soc. (London) A111, 355 (1926).
[14] See, for example, R. A. Friedel and M. Orchin, Ultraviolet Spectra of Aromatic Compounds, John Wiley and Sons, New York, Spectrograms No. 83 and 265.

It can therefore be expected that transition I of β-nitro-naphthalene is located in the same spectral region as is transition I of β-naphthylamine, i. e., close to 29500 cm^{-1} with an ϵ value of about 1300. It can further be expected that transition II of β-nitronaphthalene is located in the vicinity of 36400 cm^{-1} (2750 Å) and has an intensity of $\epsilon_{max} \sim 5000$. Actually, an examination of the β-nitronaphthalene curve shows good agreement with these predictions, as will be shown below.

(c) The absorption curve of m-nitro-nitrosobenzene. After discussing the existence of a hidden transition near 2900 Å and its interpretation, as well as that of the strong transition near 2500 Å, we now wish to show that the weak 3500 Å transition of nitrobenzene can be connected with the NO_2 group. This transition, which appears in many substituted nitrobenzenes at nearly the same position and with nearly the same intensity, has not received much attention lately. Previously, it was often connected with transition I of benzene or with the "Vorbande" of benzene[1,4] which, as is known now,[15] is the 1-0 band of transition I.

Recently Nakamoto[7] published the absorption curve of m-nitro-nitrosobenzene in alcohol in connection with his work on dichroism. m-Nitro-nitrosobenzene shows two very weak transitions of the same intensity ($\epsilon_{max} \sim 60$) at 3900 Å and 7500 Å. The first of these is at about the same location at which nitrobenzene has a transition of comparable intensity. A similar correspondence exists

[15]H. Sponer, G. Nordheim, A. L. Sklar and E. Teller, J. Chem. Phys. 7, 207 (1939).

for the 7500 Å transition for nitrosobenzene and m-nitronitroso-
benzene. This fact suggests that the 3500 Å transition of nitro-
benzene and the 3900 Å transition of m-nitro-nitrosobenzene are
related to the NO_2 group. (See also next section.) It is felt
that the evidence given in this section is in favor of our inter-
pretation of the nitrobenzene spectrum.

RECENT INTERPRETATIONS OF THE SPECTRA OF
NITROBENZENE AND NITROBENZENE DERIVATIVES

Three papers have recently been published which disagree, as
we do, with the generally accepted explanation of the 2500 Å
transition of nitrobenzene.

Doub and Vandenbelt investigated numerous para-[16] as well
as ortho- and meta-[17] disubstituted benzene derivatives in water.
They came to the conclusion that, by mono-substitution and disub-
stitution, the benzene transitions near 2600 Å, 2100 Å and 1800 Å
are generally displaced in a regular manner towards the red.
Among the substances examined were aromatic nitro-compounds; and
the spectra of nitrobenzene, the nitrotoluenes, the dinitroben-
zenes and the chloro-nitrobenzenes were interpreted in a manner
similar to that given above. The authors state, however, that the
nitro-compounds do not agree well with their correlation and that
the nitro-group seems exceptional. We believe that this conclu-

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[16]L. Doub and J. M. Vandenbelt, J. Am. Chem. Soc. 69, 2714 (1947).
[17]L. Doub and J. M. Vandenbelt, J. Am. Chem. Soc. 71, 2414 (1949).

sion is largely due to the fact that nitrophenols and nitro-
anilines were included in their investigations. These are com-
pounds for which assignments are not easy to make.

Platt's[18] interpretation of the nitrobenzene spectrum is
based on theoretical considerations which he supports with a com-
parison of the spectra of benzoic acid and nitrobenzene. He
suggests a correspondence between the nitrobenzene transitions
$\nu_{max} \sim 33000 cm^{-1}$ and $\nu_{max} \sim 40000 cm^{-1}$ with the benzene transitions
I and II. While we largely agree with his interpretation, we
believe that the n-π band in the nitrobenzene spectrum is not
hidden. It corresponds to the 3500 $\overset{o}{A}$ transition, which Platt
does not mention.

Nakamoto's[7] interpretation of the spectra of m-dinitrobenzene
and m-nitro-nitrosobenzene in alcohol solution is included here.

	NO-band	NO_2-band	π-band	δ-band
m-dinitrobenzene	--	3300 $\overset{o}{A}$ (300)	3000 $\overset{o}{A}$ (1300)	2500 $\overset{o}{A}$ (16000)
m-nitro-nitroso-benzene	7500 $\overset{o}{A}$ (60)	3900 $\overset{o}{A}$ (60)	3200 $\overset{o}{A}$ (2500)	2650 $\overset{o}{A}$ (18000)

ε_{max} in brackets.

We agree with his interpretations except that the strong
transitions at 2500 $\overset{o}{A}$ and 2650 $\overset{o}{A}$, respectively, are in our opinion
π-electron transitions.

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[18] J. R. Platt, J. Chem. Phys. 19, 101 (1951).

EXAMINATION OF THE β-NITRONAPHTHALENE CURVE
IN ISO-OCTANE

One might expect that the β-nitronaphthalene curve would show a weak transition corresponding to the one near 3500 Å found in the other aromatic nitro compounds discussed above. However, the absorption curves of Hertel[9] and of Hodgson and Hathway[10] do not show such a transition. The same result was obtained by this author after carefully measuring β-nitronaphthalene as far as 4500 Å. We are, therefore, inclined to believe that this transition is hidden, a possibility which will be investigated in a later paper. Since NO_2-compounds show unusually strong solvent effects,[4] only absorption curves in iso-octane or similar hydrocarbons should be considered for comparison purposes. The β-nitronaphthalene curves so far published were measured in absolute alcohol. This was another reason why the author felt that a new determination in a non-polar solvent was advisable. A pure sample of β-nitronaphthalene was measured therefore with a Beckman quartz spectrophotometer model DU using quartz cells of 1 cm path length and using purified iso-octane as solvent. Compared with the alcohol curve, the iso-octane curve is shifted somewhat towards the u.v. and shows a slight decrease in intensity. It was further observed that β-nitronaphthalene shows in iso-octane two well-separated transitions of fairly strong intensity.

Transition 1	$\lambda_{max} = 3420$ Å $(29200$ cm$^{-1})$	$\mathcal{E}_{max} = 2500$

Transition 2	$\lambda^a_{max} = 2920$ Å $(34300$ cm$^{-1})$	$\mathcal{E}^a_{max} = 8200$
	$\lambda^b_{max} = 3000$ Å $(33300$ cm$^{-1})$	$\mathcal{E}^b_{max} = 8000$
	$\lambda^c_{max} = 3020$ Å $(33100$ cm$^{-1})$	$\mathcal{E}^c_{max} = 8270$

	$\lambda_{min} = 3200$ Å $(31200$ cm$^{-1})$	$\mathcal{E}_{min} = 1640$

Transition 2 shows some structure which is not noticeable in alcohol solution. Position and intensity of both transitions are in good agreement with the predictions given in the second section, although the intensity of the 3420 Å transition seems somewhat too high.

A third strong transition of β-nitronaphthalene near 2600 Å, $\mathcal{E}_{max} = 25000$ corresponds apparently to the strong naphthalene transition at 2200 Å.

THE WEAK TRANSITION OF NITROBENZENE AT 3500 Å

During recent years certain weak transitions, called n-transitions, have been frequently investigated.[18-21] As the weak transition of nitro-benzene, and the corresponding weak transitions of other aromatic nitro-compounds, belong possibly to the group of these n-π transitions, it will be of interest to examine

[19] F. Halvorsen and R. C. Hirt, J. Chem. Phys. 19, 711 (1951).
[20] H. McConnell, J. Chem. Phys. 20, 700 (1952).
[21] J. H. Rush and H. Sponer, J. Chem. Phys. 20, 1847 (1952).

them further. It should, however, be mentioned that on account
of their low intensity and their closeness to a stronger transi-
tion, changes of intensity and position are often difficult to
observe.

The results published so far by various authors concerning
solvent effects contradict each other. Scheibe,[3] Dede and
Rosenberg[5] agree that the weak transition of nitrobenzene and of
the nitrotoluenes shifts towards the red when passing from hexane
to methylalcohol solution. McConnell,[20] however, observed in
s-trinitrobenzene a very small blue shift (100 cm^{-1}) of an absorp-
tion shoulder near 4000 Å, $\varepsilon \sim 20$, in passing from heptane to
water, whereas at wavelengths less than 3860 Å the entire spec-
trum underwent a strong red shift. This does not agree with the
findings of other workers who observed the weak transition of
s-trinitrobenzene at 3300 Å ($\frac{n}{1000}$ HCl),[4] 3370 Å (CCl_4)[22] and
3500 Å (alcohol).[23] It will be of interest to clarify these
contradictory statements.

NITROBENZENE AND STERIC INHIBITION OF RESONANCE

The interpretation of the nitrobenzene spectrum given above
is similar to that of the biphenyl spectrum, which was given in
a previous paper.[24] In both cases the implications are the same.

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[22] G. Briegleb and Th. Schachowskoy, Z. Phys. Chem. B19, 255 (1932).
[23] K. Nakamoto, J. Am. Chem. Soc. 74, 1739 (1952).
[24] A. Wenzel, J. Chem. Phys. 21, 403 (1953).

If our interpretation is correct, the current explanation of intensity decreases by o-methyl-substitution or similar o-substitutions in nitrobenzene and biphenyl has to be modified.

It is at present generally assumed that the strong intensity of the 2500 Å transition of biphenyl and nitrobenzene is due to resonance of the substituent with the benzene ring, producing a large increase of transition I of benzene in the case of biphenyl, and of transition I or of the NO_2 band in the case of nitrobenzene. It is further assumed that the well-known intensity decrease of the 2500 Å transition by o-methylsubstitution can be explained by the suppressing of this resonance interaction, called steric inhibition of resonance. The author believes that this interpretation is incorrect, since the 2500 Å transition of nitrobenzene and biphenyl correspond in her opinion to transition II of benzene.

During the last few years many papers have been published discussing the influence of steric inhibition of resonance on absorption curves. It may be that some of the assignments given in those papers should be reviewed on the basis of the interpretations given above. A paper along these lines is in progress.

Vapor Absorption Spectra of Light and Heavy Naphthalenes

at 2900-2500 A.[*]

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ABSTRACT

The 2900-2500A region of absorption in both light and heavy naphthalene is interpreted as an allowed $A_{1g}-B_{2u}$ transition, and the bands at 35910 and 36040 cm^{-1} are assigned as the respective 0,0 bands. Upper state frequencies of 130, 485, 710, 995, 1390, 1520, and 1600 cm^{-1} and the ground state frequencies of 195, 495, 755, 1024, and 1380 cm^{-1} in the ordinary naphthalene spectrum are correlated with previously reported Raman frequencies. A corresponding interpretation is given for the vibrational frequencies occurring in the spectrum of deuterated naphthalene. The general appearance of the spectrum is compared with recent absorption curves in solid solution by Passerini and Ross, and with crystal data obtained with polarized light. Possible occurrence of vibrationally induced "forbidden" bands is discussed.

Introduction

The near ultraviolet absorption spectra of naphthalene have been studied by many investigators. As early as 1881 the solution spectrum[1] was reported. Since then more reliable data have been published, for example, by Morton and de Gouveia,[2] Mayneord and Roe,[3] and the American Petroleum Institute.[4] The vapor spectrum was first reported by Purvis[5] in 1912. More detailed spectrograms and detailed tables were published by Henri and de Laszlo[6,7] in 1924. The absorption spectrum of the solid was

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1. W. N. Hartley, J. Chem. Soc. 39, 153 (1881).

2. R. H. Morton and A. J. A. de Gouveia, J. Chem. Soc. 137, 911 (1934).

3. W. V. Mayneord and E. M. F. Roe, Proc. Roy. Soc. A 152, 299 (1935).

4. A.P.I. Research Project 44 at N. B. S., Catalog of Ultraviolet Spectrograms. Ser. No. 87, California Research Corporation.

5. J. E. Purvis, J. Chem. Soc. 101, 1315 (1912).

6. V. Henri and H. de Laszlo, Proc. Roy. Soc. A 105, 662 (1924).

7. H. de Laszlo, Z. phys. Chem. 118, 369 (1925).

studied by Seshan,[8] Sirkar,[9] and Prikhotjko.[10,11] Both the infrared[12-14] and Raman spectra[15] of naphthalene are known.

For deuterated naphthalene, the spectroscopic data available are rather meager because many of them are in abstract or review form or unpublished (infrared,[16,17] Raman,[18,19] electronic spectra).[20,21]

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8. P. K. Seshan, Proc. Indian Acad. Sci. 3, 148 (1936).

9. S. C. Sirkar, Indian J. Phys. 10, 109 (1936).

10. A. Prikhotjko, J. Phys. (USSR) 8, 257 (1944).

11. A. Prikhotjko, Izvest. Akad. Nauk USSR, Ser. Fiz. 12, 499 (1948).

12. P. Lambert and J. Lecomte, Ann. phys. 18, 329 (1932).

13. Barnes, Gore, Liddell, and Williams, "Infrared Spectroscopy", Reinhold, New York, 1944, p. 56.

14. G. C. Pimentel and A. L. McClellan, J. Chem. Phys. 20, 270 (1952).

15. K. W. F. Kohlrausch, Ramanspektren, Akademische Verlagsgesellschaft, Becker and Erler Kom. Ges., Leipzig (1943), pp. 385-390.

16. L. Corrain, Phys. Rev. 79, 235A (1950).

17. Person, Pimentel, and Schnepp, J. Chem. Phys., in press.

18. H. Luther, Abh. Braunschweig, Wiss. Ges. 1, 33 (1949); Gorbeau, Luther, Feldmann, and Brandes, Ber. 86 (2), 214 (1953).

19. E. R. Lippincott and E. J. O'Reilly, Jr., J. Chem. Phys., in press.

20. C. D. Cooper and H. Sponer, Phys. Rev. 87, 213A (1952).

21. H. Sponer and Gertrud P. Nordheim, Discuss. Far. Soc. 9, 19 (1950).

Experimental Procedure

The naphthalene used in this research was purified by Dr. L. Corrsin. He obtained Eastman Kodak's highest purity naphthalene and refluxed it over sodium to remove a suspected thionaphthene impurity. Further purification was carried out by repeated recrystallization. Dr. Corrsin also prepared the deuterated naphthene by exchange with D_2SO_4. The sample used contained about 99% deuterium.

The optical arrangement used in this research and the method of controlling the number of molecules in the light path are the same as that used for previous studies from this laboratory. A quartz absorption cell 75 cm in length was used. A 2300 volt AC hydrogen lamp served as a light cource and an iron arc was utilized to produce a comparison spectrum. The spectrograph consisted of a 3-meter reflection grating in a modified Eagle mounting. The grating was used in the first order giving a practically linear dispersion of 5.535 A/mm. Eastman Kodak II-O and II-O U.V. spectroscopic plates were used and they were developed for five minuted in D-19 developer. The vapor pressures for the different temperatures were obtained from the measurements of Schlumberger[22] and Speranski.[23]

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22. E. Schlumberger, J. Gasbel. 55, 1257 (1912).
23. A. Speranski, Zs. Phys. Chem. 46, 74 (1903).

Experimental Results

The light and heavy naphthalene spectra were studied in dependence on their temperature and vapor pressure for temperatures between -11° and 130°C. For both compounds a few broad absorption bands are observed around 2750 to 2650A for a substance temperature of 0°C (0.006 mm Hg). At the higher temperature of 20°C (0.054 mm Hg) there is complete absorption in the above region and many diffuse bands are found between 2900 and 2500A. For a temperature of 65°C (2.65 mm Hg) many sharp bands are observed between 3100 and 2900A.

Primarily, this paper deal with the absorption system of medium intensity between 2900 and 2500A, but the absence in our spectra of the strong bands reported by Henri and de Laszlo between 2935 and 2948A should be noted. A study of the thionaphthene spectrum in our laboratory[24,25] showed that these bands as well as some weaker ones in the 2900A region were due to a thionaphthene impurity in Henri and de Laszlo's sample.

The strongest bands in the 2900-2500A region of the naphthalene spectrum are located at 35910, 35790 and 35720 cm^{-1}. These bands are diffuse and are just detectable on a spectroscopic plate for a substance temperature of 0°C (0.006 mm Hg). With increasing temperature and pressure, close lying diffuse bands appear on

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24. R. C. Heckman, Phys. Rev. 91, 242A (1953).

the red side of each band. Fig. 1 shows the fully developed band
system at 20°C (0.05 mm Hg) and here it can be seen that most of
the bands fit into three re-occurring groups which have the three
strong bands mentioned above as their band of longest wavelength.
The bands are degraded toward the red and the ultraviolet edge
of each band was measured. All of the measured bands are given
in Table I. The 2900-25 (A absorption region in the deuterated
naphthalene spectrum resembles very closely the corresponding
absorption in naphthalene. The most noticeable difference is the
shift of the 35910 cm⁻¹ naphthalene band to 36040 cm⁻¹ in the
spectrum of the deuterated sample. A print of this spectrum is
shown in Fig. 1 and the measured bands are recorded in Table II.
In both Tables I and II, columns one and two contain the wave-
lengths and wavenumbers, respectively. Column three gives the
separation from the chosen 0,0 band and column four gives inten-
sity data for different temperatures and pressures. Assignments
are given in the fifth column. Most of the wavelength measure-
ments are recorded to the nearest Angstrom because of the dif-
fuseness of the bands involved. The wavenumbers are accurate to
within 10 or 15 wavenumbers, except for those bands that are
extremely diffuse. For these extremely diffuse bands the measure-
ment may be in error by 30 cm⁻¹ or more. Under the intensity
column, estimates of the band intensity are given. They were ob-
tained from microphotometer tracings (Jarrell-Ash microphotometer)
and have been supplemented by visual estimates where necessary.

20°C   15°C

0+2×1390   0+2×1360
38720   38795

0+1390+485   0+1360+485
37795   37880

0+1390   0+1360
37300   37400

0+995   0+835
36905   36875

0+485   0+485
36395   36525

0,0   0,0
35910   36040

60°C   50°C   55°C

0-495
35415

35087
0-1024   0-2×500
34886   35055

$C_{10}H_8$ $C_{10}D_8$
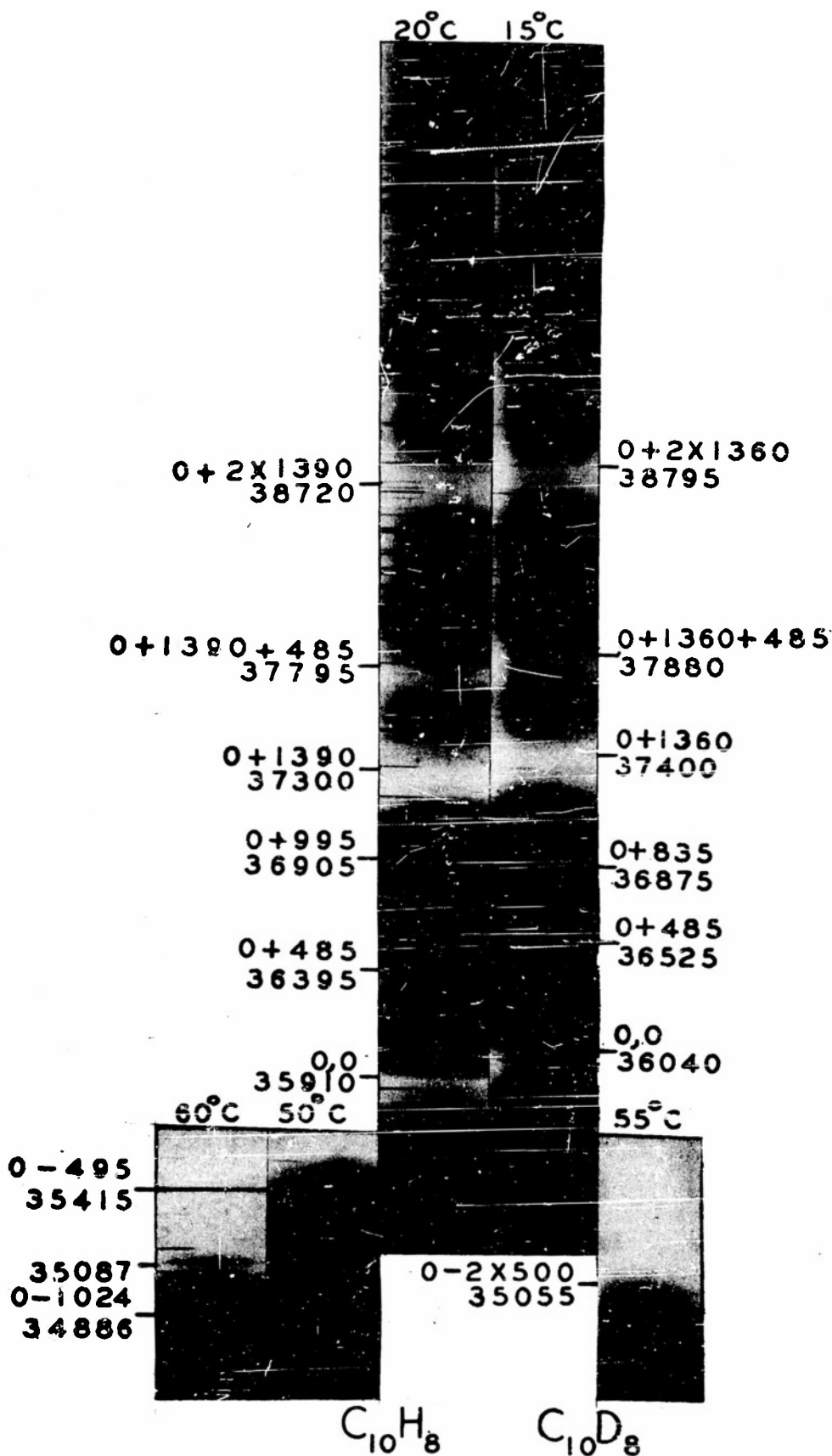
Table I
Absorption bands of naphthalene vapor in 2900 to 2500A region

Wave-length A	Wave-numbers cm-1	Separation from 0,0 Band 35910 cm-1	Intensity			Assignments
			t=70°C p=3.95 mm Hg	t=60°C p=1.83 mm Hg	t=50°C p=0.82 mm Hg	
2894.6	34537	-1373	mw	vw-d-B		0-1380 ?
93.1	555	-1355	mw-d			
92.8	558	-1352	m-d	ew		
91.9	569	-1341	m-d	ow		
91.0	580	-1330	m-d	vw		
90.0	592	-1318	m-ed	mw	vw	
88.2	614	-1296	m-d	w		
87.3	624	-1286	m-sd	w	vw	0-1380+90 ?
70.2	831	-1079		ew-d		
69.1	844	-1066		vw-d	ew	
68.1	856	-1054		vw-d	vw	
66.4	877	-1033		w-sd	vw	
65.6	886	-1024		mw-s		0-1024 ?
59	965	-945		ew-ed-B		
56.0	35004	-906			ew	
55.3	012	-898		ew-d	ew	
54.6	021	-889		vw-d	ew	
53.7	032	-878		vw-sd	ew	
52.5	047	-863		m-d	w	
51.6	058	-852		ms-d	ms	
50.8	068	-842		s-sd	ms	
50.0	077	-833		s-sd	ms	
49.2	087	-823		s-sd	ms	

Table X — Continued

Wave-length A	Wave-numbers cm⁻¹	Separation from O,O Band 35910 cm⁻¹	Intensity		Assignments
			t=20°C p=0.65 mm Hg	t=50°C p=0.82 mm Hg	
44	155	−755		ew−ed−B	0−755
30	325	−585		vw−ed−B	
23	415	−495		m−ed−B	0−495
16	475	−435		vs−vd	
13.4	534	−376		s−sd	
12.6	544	−366		s−sd	
2799	715	−195	vw−ed		0−195
98	730	−180	vw−ed		0−130−50
95	770	−140	vw−vd		0−140
94	780	−130	mw−vd		0−130;0−2x65
92	805	−105	w−vd		0−105
89	845	−65	w−vd		0−65;0−195+130
88	860	−50	vw−vd		0−50
84	910	0	s−vd ⎫		0,0
83	920	10	s−d ⎬		0+10
82	935	25	ew−vd		
77	36000	90	w−vd		0+90
75	025	115	ew−d		
74	040	130	ew−d		0+130
55	285	375	vw−d		0+485−105
53	315	405	vw−d		0+485−80
51	340	430	mw−vd		0+485−50,0+430 ?
47	395	485	mw−vd		0+485

Table I - Continued

Wave-length A	Wave-numbers cm^{-1}	Separation from O,O Band 35910 cm^{-1}	Intensity t=20 C p=0.05 mm Hg	Assignments
39	500	590	ew-ed	
37	525	615	ew-d	O+485+130
35	550	640	ew-d	O+710-65
30	620	710	ew-vd	O+710
18	780	870	ew-ed	O+995-130
13	850	940	ew-ed	O+995-50
09	905	995	w-ed	O+995
05	960	1050	ew-ed	
2696	37080	1170	ew-ed	
92	135	1225	ew-ed	
90	165	1255	vw-ed	O+1390-130
86	220	1310	m-ed	O+1390-80
84	245	1335	ms-ed	O+1390-65
83	260	1350	e-ed	O+1390-50
80	300	1390	vs-vd	O+1390
79	315	1405	m-vd	O+1390+15
76	360	1450	w-ed	O+1520-65
71	430	1520	m-ed	O+1390+130, O+1520
69	455	1545	ew-ed	O+1600-50
68	470	1560	ew-ed	
65	510	1600	vw-ed	O+1600
60	585	1675	ew-vd	
51	710	1800	w-ed	O+485+1390-80

Table I — Continued

Wave-length A	Wave-numbers cm⁻¹	Separation from 0,0 Band 35910 cm⁻¹	Intensity t=20°C p=0.05 mm Hg	Assignments
48	755	1845	ms–ed	0+485+1390–50
45	795	1885	ms–ed	0+485+1390
44	810	1900	m–ed	0+485+1390+15
40	870	1960	ew–ed	
36	925	2015	vw–ed	0+485+1390+130
29	38025	2115	ew–ed	0+710+1390
20	155	2245	ew–ed	0+995+1390–140
18	185	2275	ew–ed	0+995+1390–105
14	245	2335	w–ed	0+995+1390–50
11	290	2380	mw–ed	0+995+1390
06	360	2450	ew–ed	
2588	630	2720	m–ed	0+2x1390–80
85	675	2765	ms–ed	0+2x1390–50
82	720	2810	ms–ed	0+2x1390
79	765	2855	mw–ed	0+1520+1390–50
76	810	2900	mw–ed	0+1520+1390
55	39125	3215	w–vd	0+2x1600
52	175	3265	vw–vd	
50	205	3295	vw–ed	0+485+2x1390
46	260	3355	ew–ed	
42	320	3415	ew–ed	
2490*	40150	4240	ew–ed–B	0+3x1390; 0+1520 +1390

*Center of absorption about 200 cm⁻¹ in width.

Table II
Absorption bands of deuterated naphthalene vapor in the 2900 to 2500A region

Wave-length A	Wave-number cm⁻¹	Separation from 0,0 Band 36040 cm⁻¹	Intensity t=65°C p=0.65 mm Hg	t=55°C p=1.26 mm Hg	Assignments
2892.4	34562	−1480	ew−d	ew	
91.7	572	−1470	ew−d	ew	
90.1	591	−1450	ew−sd		
89.2	602	−1440	ew−sd		
88.3	612	−1430	ew−d		
86.8	631	−1410	ew−d		

			t=45°C p=0.52 mm Hg		
71	820	−1220	ew	ew−ed−B	
65	895	−1145	ew	ew−ed−B	
60	995	−1085	ew	vw−vd−B	
56	35000	−1035		ew−ed	0−2x500−50 ?
52	055	−985	ew	ew−ed−B	0−2x500 ?
38	225	−815	ew	ew−ed−B	
36	250	−790	ew−ed		
31	315	−725	ew−ed		
27	365	−675	ew−ed		0−500−185
24	400	−640	ew−ed		0−500−145

			t=35°C p=0.21 mm Hg		
17	490	−550	mw−ed−B	vw	0−500−50
13	540	−500	s−ed−B	mw	0−500 (491 R)
08	600	−440		vw−ed−B	0−500+50

Table II - Continued

Wave-length A	Wave-number cm⁻¹	Separation from 0,0 Band 36040 cm⁻¹	Intensity t=15°C p=0.04 mm Hg	Assignments
2788	855	-185	vw-vd	0-185
85	895	-145	vw-vd	0-145
84	910	-130	vw-vd	0-130; 0-2x65
81	950	-90	mw-vd	0-90
79	975	-65	mw-vd	0-65; 0-185+115
77	36000	-40	ms-vd	0-40
74	040	0	ms-vd	0,0
73	050	10	vw-vd	0+10
70	090	50	m-vd	0+50
65	155	115	vw-vd	0+115
62	195	155	ew-ed	0+155
51	340	300	ew-ed	0+485-185
49	365	325	ew-vd	0+485-160
48	380	340	ew-vd	0+485-145
44	430	390	vw-vd	0+485-90
42	460	420	w-vd	0+485-65; 0+420
41	470	430	vw-vd	0+485-50
37	525	485	w-vd	0+485
34	565	525	vw-vd	0+485+50
26	675	635	ew-ed	0+635; 0+485+155
22	725	685	ew-vd	0+835-145; 0+635+50
15	820	780	ew-ed	0+835-50
11	875	835	vw-ed	0+835

Table II -- Continued

Wavelength A	Wavenumber cm⁻¹	Separated from 0,0 Band 36040 cm⁻¹	Intensity t=15°C p=0.04 mm Hg	Assignments
07	930	890	vw-ed	0+835+50
00	37025	985	ew-ed	0+835+155; 0+2x485 ?
2683	260	1220	mw-ed-vB	0+1360-145
80	300	1260	m-ed	0+1360-100
79	315	1275	m-ed	0+1360-90
76	360	1320	ms-vd	0+1360-50
73	400	1360	vs-vd	0+1360
69	455	1415	s-vd	0+1360+50
66	500	1460	ms-vd	0+1500-50; 0+1360+115
63	540	1500	m-vd	0+1500
59	595	1555	mw-vd	0+1500+50
49	740	1700	mw-vd	0+485+1360-2x65
44	810	1770	m-vd	0+485+1360-65
39	880	1840	ms-vd	0+485+1360
36	925	1885	m-vd	0+485+1360+50
29	38025	1985	ew-vd	0+485+1500; 0+485+1360+155
26	070	2030	ew-vd	0+485+1500+50
15	230	2190	w-vd	0+835+1360
09	315	2275	w-vd	0+835+1500-50
06	360	2320	w-vd	0+835+1500
05	405	2365	vw-vd	0+835+1500+50
2581	735	2695	m-vd	0+2x1360-50
77	795	2755	ms-vd	0+2x1360

Table II – Continued

Wave-length Å	Wave-number cm⁻¹	Separation from 0,0 Band 36040 cm⁻¹	Intensity t=15°C p=0.04 mm hg	Assignments
74	840	2800	m-vd	0+2x1360+50
70	900	2860	ew-vd	0+1360+1500
67	945	2905	ew-vd	0+2x1500-50 ?
64	990	2950	w-vd	0+2x1500 ?
59	39080	3040	ew-vd	
50	200	3160	w-ed-B	0+485+2x1360
2488*	40180	4140	vw-ed-B	0+3x1360

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*center of broad band.

The scale used is as follows: vs-very strong, s-strong, ms-medium strong, m-medium, mw-medium weak, w-weak, vw-very weak, and ew-extremely weak. Other notations used in the intensity column to indicate the diffuseness of the band head and to designate the broad bands are: sh-sharp, sd-slightly diffuse, d-diffuse, vd-very diffuse, ed-extremely diffuse.

Discussion

The spectrum studied here represents the second absorption region of the naphthalene molecules for which an allowed transition is expected with polarization along the short axis. Since both light and heavy naphthalene have D_{2h} symmetry, the transition is of type $A_{1g} - B_{2u}$.

The strong bands at 35910 cm^{-1} in light naphthalene and 36040 cm^{-1} in heavy naphthalene suggest themselves as the respective 0,0 bands. The observed 130 cm^{-1} shift of the 0,0 band, caused by the substitution of heavy hydrogen, is due to a change in the zero-point vibrational energies. From the appearance of the spectra it is seen that all strong bands can be explained as resulting from two vibrations with upper state values of 1390 and 485 cm^{-1} in light naphthalene, and 1365 and 485 cm^{-1} in heavy naphthalene. The 1390 and 1365 vibrations occur in progressions and in combination with the 485 vibration. (See Tables I and II). There is no doubt that the 1390 has to be associated with the very strong, polarized Raman line of frequency 1380 cm^{-1} in

ordinary naphthalene[15] which had been assigned to a totally sym-
metric carbon ring vibration. The same value, namely 1380 cm^{-1},
has been found by Lippincott* and O'Reilly as a strong line in
the Raman spectrum[19] of deuterated naphthalene. Whether this
vibrational frequency does increase in the excited state of
light naphthalene and decrease in heavy naphthalene can not be
determined with certainty due to the diffuseness and broadness of
the absorption bands. In fact, the ground state frequency of the
1360 vibration could not be ascertained in the spectrum of the
heavy molecule. However, the finding of a ground state value of
only 1373 for light naphthalene is in agreement with new results
in the Raman spectrum,[19] and is there explained** as resulting
from an accidental degeneracy (Fermi degeneracy) with another
vibrational mode.

The 485 cm^{-1} frequency occurs singly excited. It is prob-
ably represented in the ground state by the bands at 35415
(light) and at 35155 cm^{-1} (heavy) giving frequencies of 495 and
500 cm^{-1}, respectively. It seems logical to associate these
frequencies with the strong Raman lines at 512 cm^{-1} (light) and
491 cm^{-1} (heavy). (The reversal in values is probably not genuine
in view of the diffuseness and broadness of the bands.) The 512
line has been reported[15] as polarized and hence was assigned to
a totally symmetric vibration. The only band that might result
from a two-fold excitation of the 485 occurs at 37025 in

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*We are grateful to Dr. Lippincott for furnishing us the data
on heavy naphthalene prior to their publication.

**Information obtained in private discussions with Drs. O'Reilly,
Lippincott, and Pimentel.

the heavy molecule, but no counterpart was found in the spectrum of the light compound. Therefore, the last assignment is considered doubtful. We will come back to the question of the selective excitation of this vibration further below.

Another vibrational frequency is represented by the bands at 36905 (Table I) and at 36875 (Table II) giving 995 cm^{-1} in the upper electronic state of light naphthalene and 835 cm^{-1} in heavy naphthalene, respectively. If the bands are associated with the vibration which produces the strong polarized Raman lines at 1022 cm^{-1}[15] and at 862 cm^{-1}[18], the latter frequencies might take part in bands on the red side of the 0,0 band. However, no such band was found in the spectrum of heavy naphthalene, and in light naphthalene, the assignment of band 34886 to an excitation of the 1022 in the ground state is uncertain because this band may belong to the weaker long wavelength transition. Nevertheless, the mentioned correlation of the 995 and 835 with the Raman values is considered correct. The 1022 cm^{-1} frequency was interpreted by Kohlrausch[15] as a totally symmetric CH deformation vibration in the plane. The observations in the two ultraviolet spectra lend support to this assignment.

There is a very weak band at 36520 cm^{-1} in light naphthalene which may be assigned to a 0-710 transition (Table I). The 710 occurs in combination with the 1380 separation. If it is taken as the upper state value of the vibration represented in the strong polarized Raman line of 762 cm^{-1}, it represents a totally

symmetric carbon ring vibration assuming the interpretation of the Raman line to be correct. The vibration may be present in the ground state in the very weak band at 35155 cm^{-1}. Bands indicating the corresponding vibration in heavy naphthalene are not obvious, but the extremely weak band at 36675 may contain the corresponding upper state vibration of 635 in heavy naphthalene.

There are several bands in both naphthalenes which contain vibrational contributions in the range 1500-1600 cm^{-1}. The interpretation of these bands does not give a complete correspondence for the two molecules but rather leads to some peculiarities which indicate that the interpretation may not be conclusive. For example, there is a medium intense band at 37430 in the light naphthalene spectrum giving a vibrational frequency of 1520 which occurs also combined with the 1390 frequency. There are the bands at 37510 and 39125 cm^{-1}, also in light naphthalene, which might be members of a 1600 progression, and there are in the spectrum of deuterated naphthalene members of a possible 1500 progression located at 37540 and 38990 cm^{-1}. The 1600, if a fundamental, could only be linked with the Raman line at 1625 which Kohlrausch had considered to be totally symmetric, and the 1520 could be linked with the medium strong 1576 Raman line assigned to class β_{1g} by Kohlrausch.[15] It is suggestive to consider the 1500 frequency in the heavy naphthalene spectrum as counterpart of the 1520 in light naphthalene, thus relating

it to the Raman line 1548 of deuterated naphthalene.[19] We
understand, however, that the tentative assignment of Kohlrausch
has to be reversed (see our footnote **). In our case, it means
that the bands connected with the 1600 vibrations---if it is a
fundamental---are longitudinally polarized.

Assignments of most of the companion bands accompanying the
main bands are uncertain since their diffuseness allows more than
one equally good assignment. However, the band at 35715 cm^{-1} in
the spectrum of ordinary naphthalene is separated from the 0,0
band by 195 wave numbers and this might represent the 191 cm^{-1}
Raman frequency. Since this Raman frequency is depolarized it
must belong to one of the three β_g vibrations. The single exci-
tation of a β_{1g} vibration will give a longitudinal transition
moment, and excitation of a $\hat{\beta}_{3g}$ vibration will give a moment per-
pendicular to the molecular plane. No moment is associated with
excitation of a β_{2g} type vibration. Now a very low-lying β_{1g}
vibration is not to be expected for naphthalene, and bands with
polarization perpendicular to the molecular plane are generally
considered unlikely for $\pi-\pi$ transitions of aromatic molecules.
Therefore, we would not discuss the assignment of the 191 sepa-
ration to a fundamental, had we not found a corresponding band
in the heavy compound 185 cm^{-1} to the red from the 0,0 band whose
value coincides well enough with a Raman frequency[19] of 180 cm^{-1}.
Of course, the 195 could represent 3x65 or 2x105 of another vi-
bration, and the 185 could be 3x65 or 2x90 correspondingly. It

should be noted that bands were observed 130 cm^{-1} and 115 cm^{-1} to the violet from the 0,0 bands in light and heavy naphthalene, respectively, and if taken as upper state values of the 195 and 185 frequencies, the 65-70 differences in the two spectra could be interpreted as 1,1 and 2,2 transitions of these vibrations. From all this we should like to interpret, although tentatively, the 195 and 185 as β_{3g} vibrations. The foregoing discussion shows the difficulties encountered in the assignment of bands occurring on the red side of the strong bands. It is a difficulty characteristic of vapor spectra of aromatic compounds.

A noticeable feature of the system is the appearance of a weak band at 90 cm^{-1} to the violet from the 0,0 band in light naphthalene and 50 cm^{-1} correspondingly in heavy naphthalene. The occurrence of similar companions of other outstanding bands is clearly recognizable in the heavy compound, but is not as distinct in the spectrum of light naphthalene. We cannot give a convincing interpretation of the 90 and 50 cm^{-1} companion bands at present.

Many bands in the region of overlap of the two electronic transitions are not discussed here (some lying beyond the range of Table I and II) because it is believed that they belong to the first weaker transition.

The vibrational frequencies determined from the 2900-2500A absorption region of both light and heavy naphthalene are collected in Table III.

Table III. Vibrational frequencies obtained from the 2900-2500A
spectral region of light and heavy naphthalene.

Light Naphthalene		Heavy Naphthalene		Symmetry
Lower state cm^{-1}	Upper state cm^{-1}	Lower state cm^{-1}	Upper state cm^{-1}	
195	130	185	115	β_{3g} ?
495	485	500	485	α_{1g}
755	710		635 ?	α_{1g}
1024	995		835	α_{1g}
	1390		1360	α_{1g}
	1600			
	1520		1500	

The analysis presented is neither complete nor entirely
satisfactory, but is believed to account for the main features
of the spectrum. The outstanding bands involve two vibrations
only, the 500 and the 1390 (1360 resp.). In fact, Prikhotjko[11]
reported only on these. Their prominence is particularly clear
from microphotometer tracings of the plates. We found a compari-
son very interesting of our plates and tracings with a very good
reproduction of the second electronic transition in naphthalene
published recently by Passerini and Ross.[25] It shows spectral
curves taken in ethanol solution at 50°C, 20°C, and -80°C, and
in 4:1 ethanol-methanol mixture at -183°C. The comparison reveals

25. R.Passerini and I.G.Ross, Journ.Scient.Instr. 30, 274 (1953).

a close resemblance of the spectrum at -183°C with the vapor spectrum. The first peak occurs in solid solution at 34700, thus establishing a shift of about 1200 cm^{-1} to the red with respect to the vapor. The strong peaks are about 1400 cm^{-1} apart and there are weaker maxima about 500 cm^{-1} toward the short wavelength side of each of the strong peaks. The 995 frequency in the vapor spectrum is, in the solid solution curve, recognizable as a step-out only.

When analyzing the spectrum it was expected to find "forbidden" bands of noticeable intensity, i.e. bands with longitudinal polarization. The proximity of the strong third electronic transition assumed to be polarized in the long axis could induce appearance of such bands through coupling with a β_{1g} vibration. Theoretically, a strong interaction of this type has been expected for the second transition of naphthalene.[26] Corresponding forbidden bands have been found in the near ultraviolet absorption spectra (first electronic transitions) of benzene derivatives, and it was observed that their appearance is slightly different from that of the regular bands of the system.[27] Unfortunately, the diffuseness of the second absorption system in naphthalene invalidates this criterion. However, excitation of a β_{1g} vibration (433 cm^{-1} upper state value) is now being held responsible[28]

26. W. Moffitt, J. Chem. Phys. 22, 320 (1954).

27. For example, S. H. Wollman, J. Chem. Phys. 14, 123 (1946).

28. Donald S. McClure, private communication.

for the strong portion of the first electronic transition. Consequently, this portion is short axis polarized (connecting the 0-1 band of Nordheim and Sponer with a β_{1g} rather than with a β_{1u} vibration). As mentioned above, a 485 cm^{-1} vibration appears strongly in the second transition of both naphthalenes. It may be added at this point that a repeated separation of 485 is also found in the overlap region of the two systems. Although the 485 occurs apparently singly excited in the second system, it was pointed out above that a correlation with the polarized Raman lines of 512 and 491 cm^{-1} is suggestive. However, from the vapor spectrum alone it cannot be ruled out entirely that a β_{1g} vibration may be involved in the bands under discussion. The 485 could represent a β_{1g} vibration, or the band 0 + 485 - 55 (Table I) might involve a separate vibration of 430 cm^{-1}. In the first case, a noticeable portion of the spectrum would have to be long axis polarized. Comparison with the crystal spectrum[10] (taken with polarized and unpolarized light) is difficult, as has been mentioned previously.[21] Considering the geometrical arrangement of the molecules in the crystal,[29] it seems that mainly short axis polarization was observed whether the electric vector of the incident light was parallel to the a or to the b axis of the crystal. The latter case gave the more intense spectra, which

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29. S. C. Abrahams, J. M. Robertson, and J. G. White, Acta Crystallographica 2, 238 (1949).

was confirmed in later work by Craig and Lyons.[30] However, new results by McClure[28] in mixed crystals of naphthalene and durene show conclusively that the second transition is predominantly short axis polarized. Taking the short axis polarization as established, the structure and appearance of the vapor spectrum indicates that the longitudinal component of the system is very weak provided that the 485 cm^{-1} separation represents a totally symmetric vibration.

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30. D. P. Craig and L. E. Lyons, J. Chem. Phys. 20, 1499 (1952).